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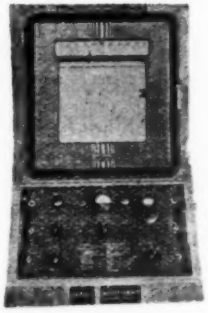

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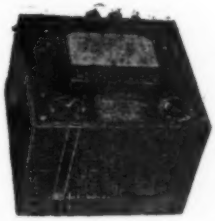

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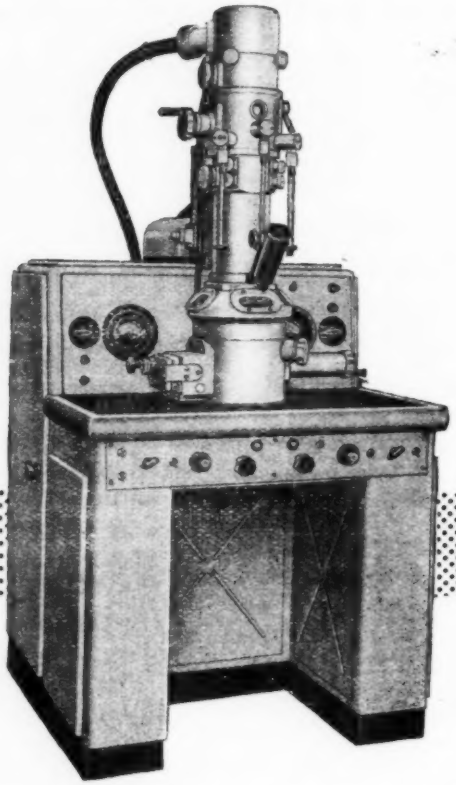

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[Joudnar. Ini Chem. Soc., Vol. 36, No 8, 1959]

MECHANISMS OF AUTOXIDATION OF THE UNSATURATED FATTY ACID ESTERS, CATALYSED BY LIGHT-SENSITISED CHLOROPHYLL*

By N. A. Khan

A sector device has been made with proper light systems, to allow intermittent illumination of the reaction vessel by visible rays of the spectrum. Studies on the oxidation reactions of methyl linoleate under catalysis of chlorophyll, sensitised by intermittent and continuous illumination, furnish clues to the non-free radical and non-chain processes involved.

In continuation of our previous studies (Khan, *Bioch'm. biophys. Acta*, 1955, **16**, 159), attempts have been made to shed more light on the non-chain processes of photo-chlorophyll oxidation of fatty acid esters. The reaction rates under intermittent illumination, as compared to those under continuous illumination (Bateman *et al.*, *Proc. Roy. Soc.*, 1948, **195A**, 376 ; Burnett *et al.*, *ibid.*, 1947, **189A**, 456, 481, 494 ; Dickinson, "The Photochemistry of Gases", Reinhold Pub. Corp., New York, 1941, p. 202), have been studied and the non-chain processes without appreciable free-radical formation have been established for these types of oxidation under catalysis of light-sensitised chlorophyll.

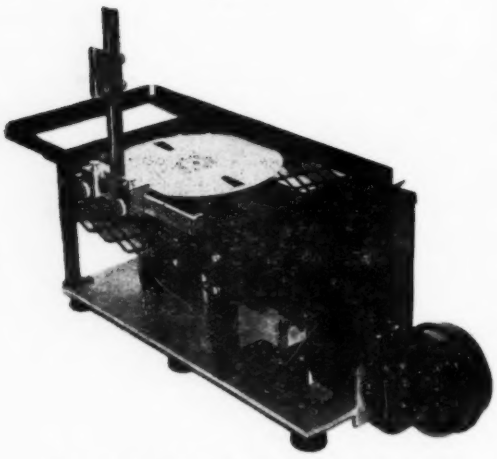
Experimental

The chlorophyll was extracted from spinach leaves (*palang*) by means of acetone (200-250 c.c./150 g. midrib-free leaves) in a Waring blender containing a small amount of $MgCO_3$. The acetone extract (500 c.c.) was diluted three times with water and extracted with purified petroleum ether (b.p. 30-60°). After washing the petroleum ether solution thoroughly with water, it was shaken portionwise with 80% methanol, saturated with petroleum ether and containing 0.01 g. oxalic acid to prevent allomerisation. To the petroleum ether solution, freed of methanol and dried with anhydrous sodium sulphate, enough dried sugar was added to absorb the chlorophyll and the mass was agitated. The sugar containing the precipitated chlorophyll was collected on top of a powdered sugar filter in a Büchner funnel. After washing the precipitate with petroleum ether chlorophyll was eluted with purified ether and the eluates dried over anhydrous sodium sulphate and stored below 0° for use. Such an ether solution may be evaporated or diluted to obtain the desired concentration of chlorophyll (a + b).

Apparatus and Methods.—The apparatus, having a sector disc for intermittent illumination, is shown in Fig. 1. The light-tight box encloses the optical system

* Some of the experiments were carried out in different laboratories of the U.S.A. during the sojourn of the author, 1947-55.

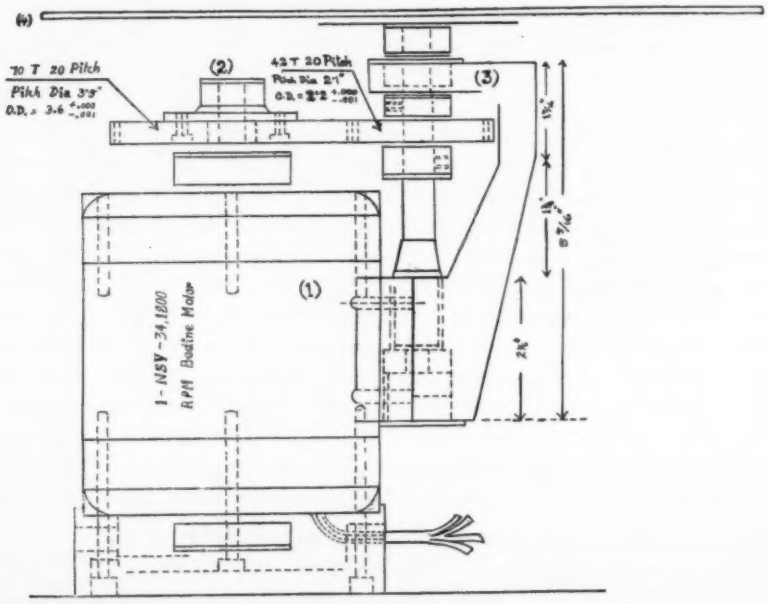
FIG. 1



Scctor dise with the rotating and illuminating arrangements.

(Fig. 3) and projects parallel light rays to the reaction flask placed above the glass bottom of the bath (Fig. 4) kept at 25°. Intermittent illumination was obtained by the use of a disc (Fig. 1) having two sectors, which was rotated at a constant speed of 3000 r.p.m. in the path of the light. The disc was made from aluminium sheet of radius 5.5 inches, and the two sectors were equally balanced on opposite edges of the disc (Fig. 1). The light from a 500 W projection lamp A (Fig. 3) passed through a pyrex cell B, with one side frosted and filled with distilled water. These light rays were made parallel by a lens C ($f = 5''$) to impinge on the front face of the mirror D placed at 45°, which reflected it through the sector opening, G; the glass bottom of the bath H; 1″ inch of water, I; and the reaction flask J (Fig. 3).

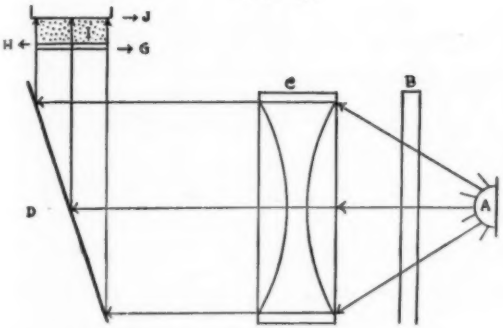
FIG. 2



Sectional sketches of the gears (2-3) in relation to synchronous motor (1) at bottom and sector disc (4) at top with descriptions recorded.

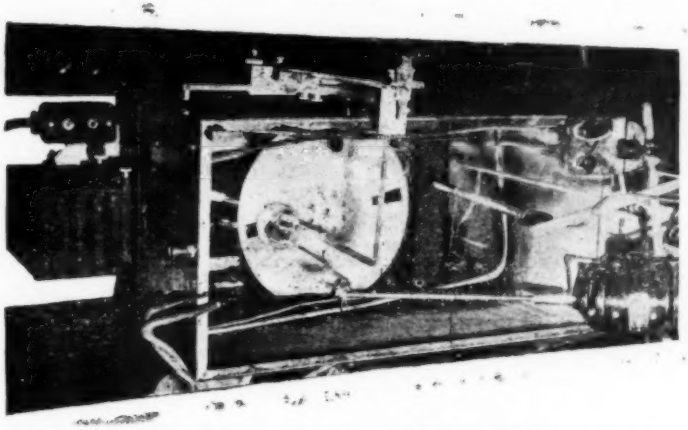
The sector disc was driven through a series of gears (Fig. 2) by a synchronous motor. The Warburg flask and manometer were modified as shown in Fig. 4 in relation to the rest of the system, the glass-bottomed bath in particular. The flask was round-bottomed (dia. 2 inches, capacity *ca.* 20 c.c.) and the side arm was considerably lengthened so as to place the reaction flask just above the sector opening. The manometer arm was attached to an adjustable system (Fig. 1 & 4), free to move parallel or perpendicular to the bath. For a control reaction, a similar system was used on an adjustable stand, not shown in the picture. The oxidation was carried out on a thin film without agitation. Methyl linoleate (1 c.c.) along with 2.5 mg. of ether-free chlorophyll was used as the substrate. In the control, 1 c.c. of purified mineral oil with the chlorophyll was employed.

FIG. 3.



Intermittent illumination and reaction systems in outline schemes

FIG. 4



Modified Warburg reaction vessel in combination with the rest of the intermittent illumination system (see Fig. 3).

DISCUSSION

In previous investigations (Khan, *loc. cit.*), complex formation of chlorophyll with oxygen, as well as with the olefinic substance having α-methylenic hydrogen next to the double bond, was found to occur.

Chlorophyll oxidation under visible light has also proceeded without chain reactions, as shown by the reaction pattern (Khan, *loc. cit.*). This has been confirmed

by oxidation under intermittent illumination in the present work. In elucidating the importance of such experiments, the preliminary theoretical considerations have been dealt with first.

In a photo-oxidation, the rate of oxidation in intermittent light depends upon the frequency of interruption if the following conditions are fulfilled :

(*a*) The reaction must be a chain process, capable of being initiated photochemically.

(*b*) The mechanism of the thermal and photo-reactions must be the same except for the initiation step.

(*c*) The photo-rate must not be directly proportional to the light intensity.

(*d*) The absorption of light must take place uniformly throughout the reaction medium.

(*e*) The interruption of the light beam must be instantaneous so that scanning of the reaction vessel does not occur.

The aim of the present investigation was to decide whether condition (*a*) was met and whether the reaction was a chain reaction. The experimental set-up was designed to comply with conditions (*d*) and (*e*). The observations during the experiment permitted decision whether conditions (*b*) and (*c*) were met. Under the circumstances, the rate in intermittent light should depend on the *frequency of interruption*. At sufficiently low speeds no radicals produced during one period of illumination survive until the next light period. Each cycle then promotes an independent reaction and the total reaction observed is the sum of these. The other limit occurs when periods of darkness are so short that no appreciable decay of radical concentration occurs. The effect of intermittent light is then the same as that of reducing the intensity to a value equal to its average per cycle. Hence, these concepts follow the original ideas of Dickinson (*loc. cit.*). Consider the reaction mixture to be illuminated through a rotating sector with an opening of $1/4$ revolution. If the sector is rotated slowly, the effect is essentially that of full illumination for $1/4$ of the time, and if the rate with continuous illumination is KI_0^n, the rate with sector in operation will be $1/4\ KI_0^n$. With sufficiently rapid rotation, the effect becomes equivalent to continuous illumination with the intensity $1/4$ and the rate will be

$$K\left(\frac{I_0}{4}\right)^n$$

Hence, the rate, R, of a photochemical reaction is related to intensity of absorbed radiation by

$$R \propto \{\lambda(I_0)\}^n.$$

Therefore in the case of intermittent illumination with intensity reduced to the portion β,

$$R_{\text{int}} \propto \{\beta\lambda(I_0)\}^n.$$

Therefore for the continuous illuminatian,

$$R_{\text{cont}} \propto \beta\{\lambda(I_0)\}^n.$$

Therefore, $$\frac{R_{int}}{R_{cont}} = \beta^{n-1}.$$

Hence, R_{int} is β^{n-1} times R_{cont}. From this evaluation, Burnette *et al.* (*loc. cit.*) and Bateman *et al.* (*loc. cit.*) adopted the idea that in the particular case where $\beta = \frac{1}{2}$ (where the light and dark periods are equal, *i.e.*, sector opening constitutes $\frac{1}{2}$ the revolution, cutting down the intensity or light duration to $\frac{1}{2}$), the rate at high frequencies is $\sqrt{2}$ times that at low frequencies, assuming $n = \frac{1}{2}$, *i.e.*, the overall rate is proportional to the square root of the intensity.

In our present experiments, the light intensity was reduced during intermittent illumination to 1/12, and so the reaction time for continuous illumination was 1/12th that of the former. This will mean that if the photochlorophyll oxidation is a chain reaction and the rate of such reaction is proportional to a power of the light intensity other than the first power, *i.e.*, $n = \frac{1}{2}$, especially as noted above, then

$$R_{int}/R_{cont} = 12^{n-1},$$

and so is equal to $\sqrt{12}$ in the case of a chain reaction.

The ratio R_{int}/R_{cont} was obtained in the present investigation by the oxidation of cottonseed oil esters and methyl linoleate at 25° without solvent under continuous illumination for 5, 10, 15, 20 and 25 minutes and intermittently for corresponding periods 12 times as long. The ratio was found to be approximately 1.0.

Hence, $$\frac{R_{int}}{R_{cont}} = 12^{n-1} = 1, \textit{ i.e.}, n = 1.$$

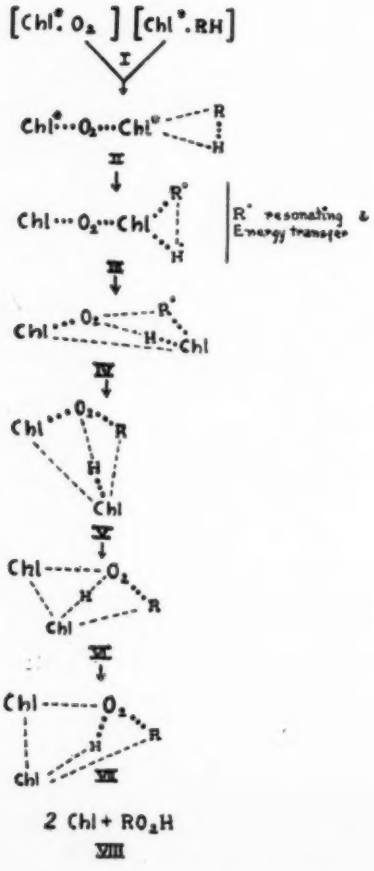
Thus, the rate is directly proportional to the intensity of light and is independent of the frequency of interruption and, hence, does not meet the requirements of a chain reaction. Further support is available from the low quantum yield (0.1), and from the fact that the rate is independent of the presence of antioxidants such as tocopherol in another series of our experiments (Khan, unpublished data). This may mean that both oxygen and the reacting substance form an intermediate complex with chlorophyll at each step of the reaction, giving rise to hydroperoxide and free chlorophyll. Furthermore, chlorophyll oxidation yields two types of peroxides, conjugated and non-conjugated, through oxidation of methyl linoleate. Hence, possibly all the three peroxidic products were formed during chlorophyll oxidation: 9- and 13- conjugated isomers, and carbon-11 non-conjugated isomer. The sensitised chlorophyll thus removes a H-atom from the carbon-11 position of the linoleate molecule and initiates the three expected radical forms through resonance of the free radicals in the C-5 system (Bolland *et al.*, *J. Chem. Soc.*, 1945, 445) of linoleate. From the foregoing observations and findings, some tentative mechanisms of chlorophyll oxidation have been proposed in line with our other concepts (Khan, *Canad. J. Chem.*, 1954, **32**, 1149).

Fig. 5 presents the general interactions of the molecules: the light-sensitised chlorophyll (Chl*), oxygen (O_2) and fatty acid ester (RH), linoleate in particular. The light-sensitised chlorophyll separately forms complexes with both O_2 and RH (fatty acid ester)

which interact (I, Fig. 5). These oxidations are obviously different from ordinary autoxidation (Khan, *loc. cit.*), in that oxygen here does not play any independent roles (II-VII). The chlorophyll-oxygen complex helps the second chlorophyll molecule polarize and activate the unsaturated centre of the fatty acid molecule (II-III). Chlorophyll pulls a H-atom away from the α-methylenic group far enough to allow resonance in the C-5 system of methyl linoleate as in the present experiment, or in the C-3 system of methyl oleate (III). The H-atom is never totally released from the chlorophyll system that also holds the free radical (R˙, II-IV). Such a controlled R˙ radical develops an affinity for O_2 in the vicinity (V). RO_2˙ in loose complexes with chlorophyll molecules in the next stage (VI) causes the existence of the H-atom to be

Mechanisms of autoxidation catalysed by light-sensitised chlorophyll.

FIG 5



Chl* ⟶ light-sensitised chlorophyll; R˙ for methyl oleate radical free for resonance;

$$-CH = CH-\overset{*}{C}H-$$
10 9 8
$$-\overset{*}{C}H-CH = CH-$$

or,

$$-\overset{*}{C}H-CH = CH-$$
11 10 9
$$-CH = CH-\overset{*}{C}H-$$

(Four isomers).

Again R˙ for methyl linoleate radical in resonance

$$-CH = CH-\overset{*}{C}H-CH = CH-$$

$$-\overset{*}{C}H-CH = CH-CH = CH-$$

$$-CH = CH-CH = CH-\overset{*}{C}H$$

(Three isomers).

quite uncertain as far as the complexing forces to itself and chlorophyll molecules are concerned. The result of these states is the association of H-atom to RO_2^- as in (VII). Two molecules of chlorophyll and one of hydroperoxide molecule are thus formed (VIII). Consequently, the three radicals resonating in the C-5 of linoleate all have chances to form three positional isomers of hydroperoxides at carbons 9, 11 and 13. Similarly, methyl oleate may yield four isomers due to resonance in the unsaturated C-4 system at carbons 8, 9, 10 and 11. Further investigations are in progress to establish the existence of these isomers through chemical and physical means.

The author wishes to thank Dr. M. Q. Khuda, Director of the Laboratories, Dacca and also Dr. Salimuzzaman Siddiqui, Director of the Pakistan Council of Scientific and Industrial Research, Karachi, for their interest and encouragement in the pursuit of this problem.

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Tejgaon, Dacca, East Pakistan.

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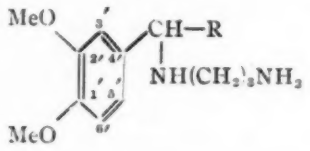
SYNTHESIS OF POSSIBLE AMOEBACIDES. PART VII

By H. N. Sharma and C. N. Kachru

Several 1-(4′-veratryl)-(*N*-γ-amino-*n*-propyl)-alkylamines having *n*-C_6H_{13}, *n*-C_7H_{15} and *n*-C_9H_{19} alkyl substitutions have been synthesised.

Synthesis of several 1-(4′-veratryl)-(*N*-γ-amino-*n*-propyl)-alkylamines (I) with alkyl substitutions as Me, Et, Pr^n, Bu^n and *n*-C_5H_{11} has been described in previous communications (this *Journal*, 1959, **36**, 247, 250). In the present communication synthesis of compounds (I) with alkyl substitutions as *n*-C_6H_{13}, *n*-C_7H_{15} and *n*-C_9H_{19} is described. These diamines will be tested for amoebacidal activity.



(I)

Experimental

4′-Veratryl-n-hexylketone.—A mixture of veratrole (50 g.), *n*-heptoyl chloride (68 g.), CS_2 (dry, 250 c.c.) and powdered $ZnCl_2$ (anhyd., 50 g.) was refluxed on a water-bath for 4 hours and then left overnight. CS_2 was removed by distillation and the residual mass decomposed by boiling with water for half an hour. The mixture was cooled and extracted with benzene. The benzene solution furnished the ketone, yield 54 g. (60%), b.p. 178-80°/4 mm.

The *semicarbazone* was crystallised from dilute alcohol in white needles, m.p. 140-41°. (Found : N, 13.79 ; OMe, 20.24. $C_{16}H_{25}O_3N_3$ requires N, 13.68 ; OMe, 20.19%).

4′-Veratryl-n-heptylketone was crystallised from dilute alcohol in silky white flakes, m.p. 50°, b.p. 180-83°/6 mm, yield 59%. The same ketone was prepared by Pathak and Pathak (this *Journal*, 1958, **35**, 789). The *semicarbazone* was crystallised from dilute alcohol in white needles, m.p. 133. (Found : N, 13.20 ; OMe, 19.23. $C_{17}H_{27}O_3N_3$ requires N, 13.08 ; OMe, 19.31%).

4′-Veratryl-n-nonylketone was crystallised from dilute alcohol in white needles, m.p. 62°, b.p. 205-208°/6 mm, yield 68%. Its preparation has also been described by

Pathak and Pathak (*loc.cit.*). The *semicarbazone* was crystallised from dilute alcohol in white prisms, m.p. 80°. (Found: N, 12.19; OMe, 17.62. $C_{19}H_{31}O_3N_3$ requires N, 12.03; OMe, 17.77%).

1-(4′-*Veratryl*)-n-*heptylamine*.—Crude 4′-veratryl-*n* hexylketoxime was reduced with metallic sodium and absolute alcohol in the usual manner, b.p. 165-68°/6 mm, yield 35%. The *picrate* was crystallised from dilute alcohol in yellow needles, m.p. 148°. The *hydrochloride* was crystallised from absolute alcohol in white prisms m.p. 226°. (Found: N, 4.93. $C_{15}H_{26}O_2NCl$ requires N, 4.87%).

1-(4′-*Veratryl*)-n-*octylamine*.—Crude 4′-veratryl-*n*-heptylketoxime was reduced in the usual manner, b.p. 170-74°/4 mm, yield 30%. The *picrate* was crystallised from dilute alcohol in yellow needles, m.p. 129°. The *hydrochloride* was crystallised from absolute alcohol in white needles, m.p. 215°. (Found: N, 4.56. $C_{16}H_{28}O_2NCl$ requires N, 4.64%).

1-(4′-*Veratryl*)-n-*decylamine* was obtained in 20% yield, b. p. 175-80°/6 mm. The *picrate* was crystallised from dilute alcohol in bright yellow needles, m.p. 113°. The *hydrochloride* was crystallised from hot water in colorless needles, m.p. 201°. (Found: N, 4.32. $C_{18}H_{32}O_2NCl$ requires N, 4.25%).

1-(4′-*Veratryl*)-(N-*cyanoethyl*)-n-*heptylamine*.—Acrylonitrile (1.8 g.) was added dropwise with constant stirring during the course of 3 hours to 1-(4′-veratryl)-*n*-heptylamine (8.7 g.), the temperature being kept below 30°. After the addition was over, stirring was continued for 5 hours and the mixture left overnight. The mixture was warmed on the steam-bath for 15 minutes and then distilled, b.p. 190-92°/6 mm, yield 6.4 g. (60%). The *picrate* was crystallised from dilute alcohol in yellow needles, m.p. 130°. The *hydrochloride* was crystallised from absolute alcohol in white flakes, m.p. 219°. (Found: N, 8.29. $C_{18}H_{29}O_2N_2Cl$ requires N, 8.22%).

1-(4′-*Veratryl*)-(N-*cyanoethyl*)-n-*octylamine* was obtained in 60% yield, b.p. 192-95°/4 mm. The *picrate* was crystallised from dilute alcohol in bright yellow needles, m.p. 125°. The *hydrochloride* was crystallised from absolute alcohol in white needles, m.p. 217°. (Found: N, 7.92. $C_{19}H_{31}O_2N_2Cl$ requires N, 7.89%).

1-(4′-*Veratryl*)-(N-*cyanoethyl*)-*n*-*decylamine* was obtained in 56% yield, b.p. 195-98°/6 mm. The *picrate* was crystallised from dilute alcohol in bright yellow needles, m p. 160° (decomp.). (Found: N, 12.32. $C_{27}H_{37}O_9N_5$ requires N, 12.17%).

1-(4′-*Veratryl*)-(N-γ-*amino*-n-*propyl*)-n-*heptylamine*.—1-(4′-Veratryl)-(*N*-cyanoethyl)-*n*-heptylamine (5 g.), dissolved in dry ether, was added portionwise to a slurry of $LiAlH_4$ (1.2 g.) and dry ether (200 c.c.). After the vigorous reaction had subsided, the reaction flask was gently warmed for 2 hours and then left overnight. Next day the excess of $LiAlH_4$ was decomposed by dropwise addition of water. The ethereal layer on distillation furnished 2.7 g. (53%) of the diamine, b.p. 170-74°/9 mm. The *picrate* was crystallised from dilute alcohol in brown needles, m.p. 143° (decomp.). The *dihydrochloride* was crystallised from a mixture of ethyl acetate and absolute alcohol, m.p. 222°. (Found: C, 56.74; H, 8.78; N. 7.28. $C_{18}H_{32}O_2N_2Cl_2$ requires C, 56.69; H, 8.92; N, 7.35%).

1-(4′-*Veratryl*)-(N-γ-*amino*-n-*propyl*)-n-*octylamine* was obtained in 52% yield, b.p. 183-85°/8 mm. The *picrate* was crystallised from dilute alcohol in yellow needles, m.p. 113°. The *dihydrochloride* was crystallised from a mixture of ethyl acetate and absolute alcohol in white needles, m.p. 207°. (Found : C, 57.63 ; H, 9.21 ; N, 7.18. $C_{19}H_{34}O_2N_2Cl_2$ requires C, 57.72 ; H, 9.11 ; N, 7.09%).

1-(4′-*Veratryl*)-(N-γ-*amino*-n-*propyl*)-n-*decylamine* was obtained in 37% yield, b.p. 194-98°/6 mm. The *picrate* crystallised from dilute alcohol in brown needles, m.p. 116°. (Found : N, 14.10. $C_{33}H_{44}O_{16}N_8$ requires N, 13.86%).

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ACTION OF DINITROGEN TETROXIDE AND ITS THERMAL DISSOCIATION PRODUCTS ON SODIUM SALTS OF ACETIC, BENZOIC, SUCCINIC AND PHTHALIC ACIDS

By Vasantrai Trambaklal Oza

The action of dinitrogen tetroxide and its thermal dissociation products on sodium benzoate, succinate, acetate and phthalate have been studied at different temperatures below 100°, to elucidate the elegant method of preparation of anhydrides of organic acids as products therefrom. A method has been devised to determine accurately all the products of reaction. The reaction is found to be temperature dependant and is therefore presumably the reaction of the salts with nitrogen dioxide. By conducting similar experiments with dinitrogen tetroxide and the anhydrides of these acids, it has been found that the anhydrides do not react with the oxides of nitrogen.

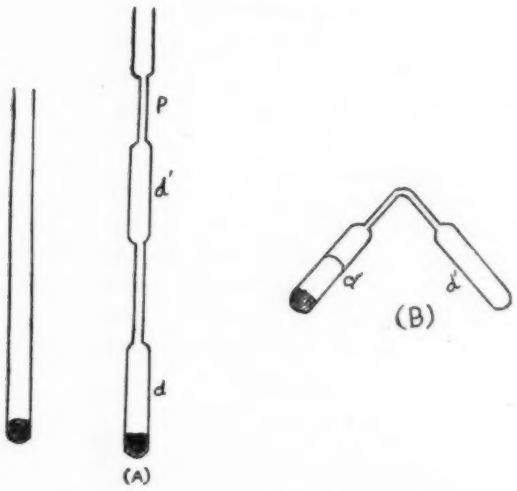
Although reactions of dinitrogen tetroxide on sodium acetate, succinate and phthalate have been studied by Rodinov and Oblisteva (*Chem. Abst.*, 1936, **30**, 4149) and by Riebsomer and Reinecke (*Chem. Rev.*, 1945, **36**, 157, 233), those of dinitrogen tetroxide and its thermal dissociation products on sodium benzoate do not seem to have been investigated in the past. This method of preparation of anhydrides of organic acids is interesting as sodium nitrate, a solid product of reaction, being an electrovalent compound, is insoluble in organic solvents and makes the separation of the anhydrides easy.

Experimental

All the sodium salts were B.D.H. chemicals, analysed for purity and found pure. The salts were dried by fusion below their decomposition temperatures, and kept in a desiccator over P_2O_5 for 24 hours before use. Particular care was taken to see that the salts and the apparatus were free from moisture. Dinitrogen tetroxide was the same as used by Oza, Oza and Thakar (*J. Chem. Soc.*, 1955, 2457). The experimental technique was the same as recorded previously (Oza, this *Journal*, 1956, **33**, 911) with the following modification in Fig. 1 shown there. The tube d (Fig. 2, *loc. cit.*), containing a known weight of sodium salt, was drawn to capillary at two places as shown in Fig. 1 'A' (this paper), and sealed at 'Z' in Fig. 1 (*loc. cit.*). The apparatus was evacuated, tested for any leak, and liquid dinitrogen tetroxide drawn into it to be collected over the contained sodium salt, in finely powdered ice. The portion shown under 'A' was then detached from the apparatus by being sealed up at 'p'. This was then bent to the form of inverted 'V' as shown in Fig. 1 'B', the portion 'd' being immersed in ice-cold water during the operation. 'B' was wiped clean and weighed. In all the experiments at 30°, the apparatus, made up in this way, was kept at that temperature for the stipulated periods of time. Such a technique was found essential, especially in reactions with sodium acetate as acetic anhydride is a liquid. At the end of the experiment, the limb 'd' was maintained at the temperature of experiment, but the limb 'd'' was cooled to less than −20° by being immersed in an

intimate freezing mixture of ferric chloride and ice. On doing this the liquid in 'd' distilled off into 'd'', leaving a negligible quantity of nitrous fumes in 'd'. 'd'' was then detached from 'd'' by being drawn out at the bent capillary. Both 'd' and 'd'' were wiped clean and weighed. 'd' was then opened in *vacuo* as in Fig. 3 (Oza, *loc. cit.*) when only one or two tiny bubbles were seen formed and absorbed in the alkali. The alkali solution showed the presence of only traces of nitrite and nitrate, as determined by micro-analysis as their quantity never exceeded 1×10^{-4} g. The solution did not respond to any test for acetate ion.

FIG. 1



The tube 'd'' was opened in 10 c.c. of CCl_4 kept under a 5 c.c. layer of potash lye (*d* 1.248). The assembly for this purpose was the same as in Fig. 1 (Oza, *Anal. Chem.*, 1957, **29**, 452). The assembly was kept at a low temperature and the tube 'd'' opened in CCl_4. Excepting when the quantity of dinitrogen tetroxide was large, the tetrachloride layer remained colorless, and when it became coloured, it was heated in contact with the alkali to 60-70° till it became colorless. The alkali layer was then carefully withdrawn and the tetrachloride repeatedly washed with pure water till free of alkali. The tube 'd' was freed of CCl_4, cleansed, dried and weighed. This subtracted from the first weight provided the weight of its contained liquid. Nitrite was determined by standard $KMnO_4$ and total nitrate, by reduction with Devarda's alloy. From nitrite and nitrate, dinitrogen tetroxide and dinitrogen trioxide were calculated and this subtracted from the weight of the liquids in 'd'' furnished the weight of acetic anhydride formed.

The broken glass pieces of the tube 'd' were carefully collected, washed, cleaned, dried and weighed to obtain the weight of the solid it previously contained. The solid was dissolved in distilled water, made up to 100 c.c. and aliquot volumes used for determining the acid (formed from the anhydride and water) and the nitrate, and

TABLE I

Expt No.	Temp.	Period of contact (hrs.).	Subst. taken (g.).	Wt. of N_2O_4 at start (g.).	Wt. of solid residue in (d') (g.).	Wt. of liquid products of reaction in 'd'' (g.).	$NaNO_3$ formed. (g.).	Anhydride formed (g.).	Unchanged substance (g.).	Substance used up (g.).	N_2O_4 left (g.).	N_2O_4 consumed. (g.).	N_2O_3 formed. (g.).	Ratio column 11 : 13.	Ratio column 11 : 8.	Ratio column 11 : 9.	Ratio column 11 : 14.
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	(*a*).	System : sodium acetate + liquid dinitrogen tetroxide.															
1.	30°	48	0.0300	0.3481	...	...	0.0018 (0.211)	...	0.02826	0.00174 (0.211)	0.34615	0.00195 (0.212)	0.00081 (0.106)	1 : 1	1 : 1	...	2 : 1
2.	30°	720	0.0500	0.3428	0.0505	0.3419	0.0130 (1.53)	0.0077 (0.754)	0.03746	0 01254 (1.53)	0.3283	0 01450 (1.576)	0.00587 (0.768)	1 : 1	1 : 1	2 : 1	2 : 1
3.	30°	720	0.1029	0.5295	0.1040	0.5285	0.02987 (3.51)	0.0180 (1.76)	0.07410	0 02881 (3.515)	0.4970	0.0325 (3 ·32)	0.01352 (1 78)	1 : 1	1 : 1	2 : 1	2 : 1
	(*b*).	System : sodium benzoate + liquid dinitrogen tetroxide.															
4.	30°	120	0.0500	0.3451	0.05283	0.3426	0.00443 (0.53)	0.0059 (0.261)	0.04247	0.00753 (0.53)	0.3403	0 0048 (0.521)	0.0020 (0.263)	1 : 1	1 : 1	2 : 1	2 : 1
5.	30°	168	0.0700	0.3574	0.07710	0.3510	0.01063 (1.25)	0.01435 (0.635)	0.05212	0.01788 (1.25)	0.3459	0.01150 (1 25)	0.00475 (0 625)	1 : 1	1 : 1	2 : 1	2 : 1
	(*c*).	System : sodium succinate + liquid dinitrogen tetroxide.															
6.	30°	24	0.0500	0.3120	0.0588	0.3035	0.01350 (1.58)	0.0078 (0.78)	0.03757	0.01243 (0.767)	0.2975	0.01450 (1.57)	0.00598 (0.787)	1 : 2	1 : 2	1 : 1	1 : 1
7.	30°	168	0.0501	0 3159	0.0769	0.2890	0.0425 (5.0)	0.0248 (2.48)	0.0096	0.0405 (2.5)	0.2698	0 04610 (5.01)	0.0185 (2 43)	1 : 2	1 : 2	1 : 1	1 : 1
8.	30°	720	0.0490	0.3412	0.0802	0.3100	0.04900 (5.96)	0.0291 (2.91)	0.0021	0.0469 (2.908)	0.2871	0 0541 (5.88)	0.0228 (3.00)	1 : 2	1 : 2	1 : 1	1 : 1
	(*d*).	System : sodium phthalate + liquid dinitrogen tetroxide.															
9.	30°	24	0.0510	0.3015	0.0673	0 2857	0.0250 (2.94)	0.0215 (1.45)	0.0208	0.0302 (1.44)	0.2744	0.0271 (2.94)	0.0112 (1.47)	1 : 2	1 : 2	1 : 1	1 : 1
10.	30°	168	0.0501	0.2850	0.0735	0.2610	0.0371 (4.36)	0.0309 (2.09)	0.0055	0.0446 (2.14)	0.2450	0.0400 (4.34)	0.0165 (2.17)	1 : 2	1 : 2	1 : 1	1 : 1
11.	30°	720	0.0500	0.3619	0.0730	0.3385	0.0368 (4.33)	0.0302 (2.04)	0.0060	0.0440 (2.08)	0.3224	0.0395 (4.28)	0.0165 (2.17)	1 : 2	1 : 2	1 : 1	1 : 1

Note :-Figures in the bracket represent the g. mol. quantities and these are to be multiplied by 10^{-4}.

TABLE II

Expt. No.	Temp.	Period of contact (hrs.).	Subst. taken (g.).	Wt. of N_2O_4 at start (g.).	Wt. of solid residue (g.).	$NaNO_3$ formed (g.).	Anhydride formed (g.).	Unchanged subst. (g.).	Subst. used up (g.).	N_2O_4 left (g.).	N_2O_4 consumed (g.).	N_2O_3 formed (g.).	Ratio column 10 : 12.	Ratio column 10 : 7.	Ratio column 10 : 8.	Ratio column 10 : 13.
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
	(*a*). System: sodium benzoate + nitrogen dioxide.															
1.	40°	½	0.1012	0.2590	0.1210	0.02987 (3.41×10^{-4})	0.0400 (1.77×10^{-4})	0.05113	0.0506 (3.51×10^{-4})	0.2259	0.0331 (3.6×10^{-4})	0.0130 (1.71×10^{-4})	1 : 1	1 : 1	2 : 1	2 : 1
2.	50°	½	0.1010	0.3190	0.1351	0.0507 (5.96×10^{-4})	0.0680 (3.03×10^{-4})	0.01510	0.08590 (5.96×10^{-4})	0.2639	0.0552 (6.00×10^{-4})	0.0228 (3.00×10^{-4})	1 : 1	1 : 1	2 : 1	2 : 1
3.	60°	½	0.1200	0.3489	0.1620	0.06410 (7.54×10^{-4})	0.0846 (3.74×10^{-4})	0.01220	0.1078 (7.48×10^{-4})	0.2604	0.0685 (7.44×10^{-4})	0.02866 (3.77×10^{-4})	1 : 1	1 : 1	2 : 1	2 : 1
	(*b*). System: sodium succinate + nitrogen dioxide.															
4.	40°	½	0.1040	0.2431	0.1100	0.00938 (1.103×10^{-4})	0.0055 (0.55×10^{-4})	0.09512	0.00888 (0.548×10^{-4})	0.2376	0.0102 (1.108×10^{-4})	0.0042 (0.552×10^{-4})	1 : 2	1 : 2	1 : 1	1 : 1
5.	50°	½	0.1029	0.2572	0.1130	0.0162 (1.90×10^{-4})	0.0098 (0.98×10^{-4})	0.0870	0.0159 (0.956×10^{-4})	0.2396	0.0176 (1.93×10^{-4})	0.00748 (0.984×10^{-4})	1 : 2	1 : 2	1 : 1	1 : 1
6.	60°	½	0.1030	0.3021	0.1211	0.0286 (3.36×10^{-4})	0.0168 (1.68×10^{-4})	0.0757	0.0273 (1.685×10^{-4})	0.2710	0.0311 (1.631×10^{-4})	0.0128 (1.63×10^{-4})	1 : 2	1 : 2	1 : 1	1 : 1
7.	70°	½	0.1011	0.2893	0.1271	0.0410 (4.82×10^{-4})	0.0242 (2.42×10^{-4})	0.0619	0.0392 (2.42×10^{-4})	0.2445	0.0448 (4.87×10^{-4})	0.0185 (2.43×10^{-4})	1 : 2	1 : 2	1 : 1	1 : 1
8.	80°	½	0.1000	0.3603	0.1281	0.045 (5.3×10^{-4})	0.0264 (2.64×10^{-4})	0.0570	0.0430 (2.65×10^{-4})	0.3135	0.0468 (5.08×10^{-4})	0.0204 (2.68×10^{-4})	1 : 2	1 : 2	1 : 1	1 : 1
	(*c*). System: sodium phthalate + nitrogen dioxide.															
9.	40°	½	0.1002	0.3101	0.1114	0.01765 (2.07×10^{-4})	0.0150 (1.01×10^{-4})	0.07875	0.02145 (1.02×10^{-4})	0.2907	0.0194 (2.1×10^{-4})	0.00795 (1.04×10^{-4})	1 : 2	1 : 2	1 : 1	1 : 1
10.	60°	½	0.1000	0.2801	0.1170	0.0248 (2.91×10^{-4})	0.0210 (1.41×10^{-4})	0.0712	0.0288 (1.37×10^{-4})	0.2540	0.0270 (2.96×10^{-4})	0.0111 (1.46×10^{-4})	1 : 2	1 : 2	1 : 1	1 : 1
11.	80°	½	0.1001	0.3299	0.1341	0.0533 (6.27×10^{-4})	0.0451 (3.04×10^{-4})	0.0357	0.0644 (3.00×10^{-4})	0.2727	0.0572 (6.21×10^{-4})	0.0238 (3.13×10^{-4})	1 : 2	1 : 2	1 : 1	1 : 1
12.	100°	½	0.1000	0.2350	0.1460	0.07250 (8.53×10^{-4})	0.0613 (4.14×10^{-4})	0.0122	0.0878 (4.18×10^{-4})	0.1565	0.0785 (8.53×10^{-4})	0.0324 (4.26×10^{-4})	1 : 2	1 : 2	1 : 1	1 : 1

Note :-Figures in the bracket represent the g. mol. quantities.

the weight of the anhydride determined in the case of succinate, benzoate and phthalate. It was observed that when no nitrous fumes remained absorbed on the solid residue in the experiments with acetate, succinate and phthalate quite a noticeable amount remained absorbed in experiments on sodium benzoate, which in consequence looked bright yellow. The nitrous fumes were removed and absorbed in alkali either by maintaining vacuum or by applying hyvac pump to the system through the alkali.

The technique used in the experiments at temperatures higher than 30° was the same as used by Oza (*loc. cit.*, 1956). The substance under investigation was allowed to remain in contact with the nitrous gases for half an hour only. After this the temperature was reduced to 0° as the rate of reaction was negligible at 0°, and the nitrous fumes were absorbed out in alkali solution. In experiments with sodium benzoate at 60°, sodium succinate at 80° and sodium phthalate at 100°, duplicate sets of experiments were performed. The anhydrides formed needle-shaped crystals in the empty portion of the reaction tube, and these were carefully collected and their melting points determined. A known weight of anhydride was then dissolved in water (hot if necessary) and the solution titrated with a standard alkali solution to confirm the presence of the anhydride. Nitrite was not present in any of these experiments. Nitrate was determined as usual. The total weight of the sodium nitrate and the anhydride, subtracted from the total weight of the solid residue (which was weighed), furnished the weight of unchanged sodium salt. The results are shown in Tables I and II. Similar experiments were performed with pure anhydride in 'd' in place of the sodium salts. It was found that the colour of the liquid dinitrogen tetroxide did not show the slightest change after thirty days of contact, and the anhydride was recovered unchanged. No reaction was seen in any of the experiments up to 60° with benzoic anhydride, up to 80° with succinic anhydride and up to 100° with phthalic anhydride.

Discussion

In all the experiments in Table I, which were performed at 30°, the dinitrogen tetroxide preserved its liquid character as it was in the system under the pressure of its own vapour. The least period of contact of the sodium salts and the liquid dinitrogen tetroxide was 24 hours, and this increased to 720 hours in some experiments. It was observed that with the salts of monobasic acids, there was practically very little reaction in 24 hours, the colour of dinitrogen tetroxide remaining unchanged and the mass of the sodium salt remaining also unaltered (up to fourth place of decimal). When the reaction was carried out at constant temperatures for varying periods of time, it was observed that the amount of reaction increased appreciably with time, and that although a large amount of dinitrogen tetroxide was present in the system, the whole of the salt was not used up in 720 hours. On the other hand, in the case of salts of dibasic acids, the reaction was observed within half an hour only. Table II records the results at temperatures higher than 30°. In all these experiments (performed in different apparatus ; vide Oza, Oza and Thakar, *loc. cit.*), dinitrogen tetroxide was no longer present in the liquid state, and the reaction was appreciable in half an hour with sodium benzoate at 40°. In all these experiments the mass of the sodium salts

Note :-Figures in the bracket represent the g mol. quantities.

and the period of contact were constant, only the temperatures were varied. It was seen that even a rise of 10° in temperature had a very appreciable effect on the extent of the reaction, and yet in no case was the reaction completed even at 100°. Both the sodium salts and dinitrogen tetroxide were present in appreciable amounts at the end of half hour. and the reaction was therefore probably still in progress when the experiment was stopped.

The outstanding observation of this work is that the reaction is temperature dependant. It would therefore appear that the reacting species are not the molecules of dinitrogen tetroxide, but those of nitrogen dioxide formed as $N_2O_4 \rightleftharpoons 2NO_2$ with rise of temperature from 30° to 100° as this dissociation becomes complete at 120°. The reaction is dependent on the elimination of one Na_2O between two COONa groups and is naturally less pronounced therefore with the salts of monobasic acids. It can be expected that the reaction should become more pronounced as the number of carbon atoms between the COONa groups in a molecule increases. The reaction, as far as dinitrogen tetroxide is concerned, is that for every two molecules of dinitrogen tetroxide used up, one molecule of dinitrogen trioxide is formed, as for instance, as

$$2N_2O_4 \longrightarrow N_2O_5 + N_2O_3 \longrightarrow 2NO_2 + O_2 + N_2O_3$$

seems to proceed by oxygen becoming attached to Na_2O, formed by the rupure of the salt molecule. This is followed by reaction between Na_2O_2 and NO_2 as

$$Na_2O_2 + 2NO_2 \longrightarrow 2NaNO_3.$$

Thus, the overall reaction appears to be

$$2RCOONa + 2N_2O_4 \longrightarrow \begin{matrix} RCO \\ RCO \end{matrix}\!\!>\!O + 2NaNO_3 + N_2O_3.$$

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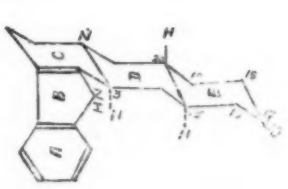
STUDIES ON STEREOCHEMICAL REACTIONS IN HETEROCYCLIC COMPOUNDS. PART I. STEREOSPECIFIC REDUCTION OF YOHIMBONE AND RAUWOLSCONE

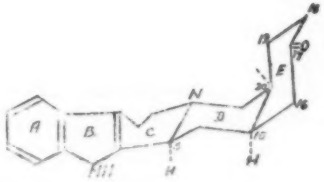
By Mrs. A. Chatterjee and S. Ghosal

Reduction of rauwolscone and yohimbone by sodium borohydride and lithium aluminium hydride affords only one epimeric alcohol, viz., *allo*yohimbol and *epi*yohimbol respectively (in almost quantitative yield), the hydroxyl group being found to be oriented equatorially. But with aluminium *iso*propoxide yohimbone produces both the epimeric alcohols (yohimbol and *epi*yohimbol), whereas rauwolscone yields with this reagent only *allo*yohimbol. Mechanism of these reactions has been discussed.

Heterocyclic ketones on reduction with complex metal hydrides are known to yield epimeric alcohols (N.G. Gaylord, "Reduction with Complex Metal Hydrides", Interscience Publishers, Inc., New York, 1956). With a view to ascertaining the possibility of such reduction with yohimbone (I) and rauwolscone (II), these ketones have been prepared from the Rauwolfia alkaloids- yohimbine and rauwolscine (α-yohimbine)-by their Oppenauer oxidation (Chatterjee, Pakrashi and Werner, *Fortsch. der Chem. Org. Naturstoffe*, 1956, **13**, 329). These heterocyclic ketones (I) and (II) were treated with sodium borohydride, lithium aluminium hydride as also with aluminium *iso*propoxide. Studies on these reactions and their mechanism are described in this communication.



(I)



(II)

Dauben, Fonken and Noyce (*J. Amer. Chem. Soc.*, 1956, **78**, 2579, 3752) have shown that reduction of alkyl *cyclo*hexanones affords increasing proportions of the axial (less stable) isomers as the reagent is changed in the order : $LiAlH_4$, $NaBH_4$ and $Al(OPr^i)_3$. An increasing 'effective size' of reducing moiety is presumed in the above order, and these reagents favour attack from the least hindered side of the carbonyl group. In this case "steric approach control" plays an important role compared with the molecular energetics of product formation ("product development control"). The latter effect is due to the ease of formation of the organo-metallic complex between the carbonyl group and the hydrides.

The results obtained in the present study with yohimbone and rauwolscone (the unhindered ketones) are in excellent agreement with the above statement of Dauben

et al (*loc. cit.*). As the carbonyl groups in yohimbone and rauwolscone are unhindered, attack by a small reagent from either side of the molecule is equally favoured. Similar studies in tropinone with lithium aluminium hydride in ether and sodium borohydride in moist methanol (Beckett, Harper and Watts, *Chem. & Ind*, 1957, 633) reveal that an axial approach of the attacking reagent resulting in the introduction of a hydrogen atom in an axial position with the formation of an equatorial hydroxyl group is the favoured reaction. This has been found to be true also in yohimbone and rauwolscone. The former was reduced with sodium borohydride (in moist methanol) as also with lithium aluminium hydride (in ether) and in both the cases a single compound, *epi*yohimbol, m p. 248-49° (decomp.) (Witkop, *Annalen*, 1943, **554**, 83), was obtained in almost quantitative yield. This *epi*-alcohol has been found to be chromatographically homogeneous and the infra-red spectrum of the compound has shown absorption peak at 1040 cm^{-1}, indicating that the hydroxyl group in this compound is equatorial. Rauwolscone under similar conditions furnished a single compound, *allo*yohimbol, m.p. 212° (decomp.) (Le Hir, Janot and Goutarel, *Bull. Soc. Chim.*, 1953, 1027) in theoretical yield. This alcohol is a homogeneous product as evidenced from its paper chromatogram, and the infra-red spectrum of the compound indicates the equatorial orientation of the hydroxyl group. Both yohimbone and rauwolscone therefore, on treatment with sodium borohydride or lithium aluminium hydride, undergo stereospecific reduction, giving rise to only one epimer where the hydroxyl group has the equatorial conformation.

Witkop (*loc. cit.*) studied the Meerwein-Ponndorf-Verley reduction of yohimbone with aluminium propoxide^i in propanol^i and isolated two epimeric alcohols from reduction products, viz., yohimbol, m.p. 243° (hydroxyl group being axial) and *epi*-yohimbol, m.p. 258° (with equatorial hydroxyl). Le Hir *et al.* (*loc. cit.*) repeated this experiment with both yohimbone and rauwolscone (α-yohimbone). From yohimbone they could isolate the same two isomers obtained by Witkop (*loc. cit.*) and these were resolvable by chromatography over alumina. But rauwolscone on treatment with aluminium propoxide^i in propanol^i behaved differently. It afforded only one stable epimeric alcohol, viz., *allo*yohimbol, m.p. 223-25°, where the hydroxyl function is only equatorial (I.R. peak near 1040 cm^{-1}). This observation has also been confirmed by the present authors.

It therefore appears from the formation of thermodynamically stable epimer, *allo*yohimbol, from rauwolscone that 'product development control' is the sole operative factor during such reduction. Dauben's suggestion (*loc. cit.*) regarding the mechanism of the formation of epimeric alcohols from their corresponding ketones (hindered) by aluminium propoxide^i reduction does not appear to be valid in the unhindered system, like yohimbone. In the opinion of the present investigators, such a variation is presumably due to the fact that it is not the 'steric approach control' factor but equilibrating capacity of aluminium propoxide^i in propanol^i (Doering and Aschner, *J. Amer. Chem. Soc.*, 1949, **71**, 838) (under reflux conditions) which is responsible for equilibration of yohimbone reduction products.

EXPERIMENTAL

Reduction of Yohimbone with Sodium Borohydride.—To a well-cooled solution of yohimbone (0.5 g.) in moist methanol (100 c.c.) a solution of sodium borohydride (2.5 g.) in the same solvent (20 c.c.) was slowly added and the solution kept at room temperature overnight. After removing the solvent the residue was decomposed with ice-cold water (10 c.c.) and extracted with ether (50 c.c. × 5). Ether extract was washed with water, dried and the solvent was removed, yielding a residue of 0.48 g. (96%).

The residue (100 mg.) was dissolved in acetone (8 c.c.) and chromatographed through Brockmann alumina (20 g.). Eluents (a mixture of acetone and methanol) were collected in fractions of 25 c.c. each (Table I).

TABLE I

Eluents.	Fractions collected.	Residue.
Acetone (98%)—methanol (2%)	1–3	Negligible
Acetone (95%)—methanol (5%)	4–7	85 mg., m.p. 246-48° (decomp.)
Acetone (80%)—methanol (20%)	8–10	Nil

Fractions (4–7) on crystallisation from acetone furnished pure *epi*yohimbol, m.p. 248-49° (decomp.). (Found : C, 76.64 ; H, 8.32 ; N, 9.61 Calc. for $C_{19}H_{24}ON_2$: C, 77.03 ; H, 8.11 ; N, 9.49%). The compound showed $[\alpha]_D^{28}$ −72°.5 (CH_3OH) and I.R. absorption peak at 1040 cm^{-1}.

Reduction of Yohimbone with Lithium Aluminium Hydride.—To a well-cooled solution of yohimbone (200 mg.), kept well-stirred in dry ether (30 c.c.), a slurry of lithium aluminium hydride (200 mg.) in the same solvent (25 c.c.) was slowly added. Stirring was then continued for 2 hours on a steaming water-bath. After the reaction was over, the slurry was cooled and decomposed with ice-cold 10% HCl (20 c.c.) ; the ether layer was separated, washed with sodium bicarbonate solution and then with water. After removing the solvent a residue (170 mg.) (yield 85%) was left, m.p. 248-50° (decomp.). It was crystallised from acetone, m.p. 249-51° (decomp.). (Found : C, 76.79 ; H, 8.27 ; N, 9.31. Calc. for $C_{19}H_{24}ON_2$: C, 77.03 ; H, 8.11 ; N, 9.49%). $[\alpha]_D^{28}$ −75° (CH_3OH). I.R. absorption peak at 1035 cm^{-1}.

Acetylepiyohimbol.—*epi*Yohimbol (100 mg.) was dissolved in acetic anhydride (2 c.c.) and two drops of pyridine were added to this solution. The mixture was then refluxed over an oil-bath for 4 hours. The dark coloured solution was cooled and poured into crushed ice when silky needles separated. These were filtered and crystallised from acetone, m.p. 244-45° (decomp.). (Found : C, 74.32 ; H, 7.53 ; N 7 90. Calc. for $C_{21}H_{26}O_2N_2$: C, 74.55 ; H, 7.69 ; N, 8 29%). I.R. absorption peaks at 1240 cm^{-1} (single peak for equatorial acetoxy) and at 1709 cm^{-1} (-O-CO).

Reduction of Rauwolscone with Sodium Borohydride and Lithium Aluminium Hydride.—Rauwolscone was similarly reduced (*vide supra*) with sodium borohydride in moist methanol and lithium aluminium hydride in dry tetrahydrofuran when *allo*-yohimbol was obtained as the sole reaction product. It was crystallised from acetone

(yield 90%), m.p. 212-14° (decomp., uncorr.). (Found : C, 76.61 ; H, 8.41 ; N, 9.58. Calc. for $C_{19}H_{24}ON_2$: C, 77.03 ; H, 8.11 ; N, 9.49%). *allo*Yohimbol showed $[\alpha]_D^{28}$-112° (CH_3OH) and I.R. absorption peak at 1038 cm^{-1}.

allo*Yohimbol Hydrochloride*.—To an ethereal solution of *allo*yohimbol (0.1 g.) dry HCl gas was passed till saturation. The solvent was removed when a gummy residue was left. The latter on crystallisation from absolute alcohol yielded *allo*yohimbol hydrochloride (45 mg.), m.p. 252-55° (decomp., uncorr.). (Found : N, 8.21. $C_{19}H_{24}ON_2$-HCl requires N, 8.42%).

allo*Yohimbol Picrate*.—To an alcoholic solution of *allo*yohimbol (30 mg.) HCl (conc., 1 drop) was added. A saturated solution of picric acid (20 mg.) in alcohol was poured slowly to this solution. An immediate change in colour (from yellow to brown) was noticed. The solution was subsequently concentrated when needles of *allo*yohimbol picrate separated. On recrystallisation from alcohol these yielded a pure sample, m.p. 238-39° (decomp.). (Found : N, 13.52. $C_{19}H_{24}ON_2.C_6H_3O_7N_3$ requires N, 13.33%).

The Meerwein-Ponndorf-Verley reduction of yohimbone and rauwolscone with aluminium propoxide[5] and propanol[6] was carried out, following essentially the same procedure as that of Le Hir *et al.* (*loc. cit.*).

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ULTRAVIOLET ABSORPTION AND ROTATORY DISPERSION OF *o*-, *m*- AND *p*-CHLORO- AND -BROMOPHENYL CAMPHOR-*β*-SULPHONATES

By S. K. Vasistha and S. Ramagopala Sarma

The ultraviolet absorption spectra of *o*-, *m*- and *p*-chloro- and -bromophenyl camphor-*β*-sulphonates (*d*- and *dl*-) have been taken in ethyl and methyl alcohol respectively. The compounds exhibit two bands, λ_{max} ; the chloro esters at 266 and 225 mμ, and the bromo esters at 267 and 228-231 mμ. The rotatory dispersion of the dextro compounds has been studied in ethyl alcohol, methyl alcohol and chloroform for 13 wave-lengths (λ=6708 – 4358Å). The rotatory dispersion can be expressed by Drude's *one term* equation with 'characteristic' wave-lengths, λ_0, varying from 2861 to 3627Å and thus differing much from the observed absorption bands. It could also be expressed by Drude's *two-term* equation in which the two absorption bands are used for the two 'characteristic' wave-lengths.

The present communication is an extension of our previous study on compounds of similar nature, *o*-, *m*- and *p*-nitrophenyl camphor *β*-sulphonates (*d*- and *dl*-) (Vasistha and Sarma, this *Journal*, 1959, **36**, 413).

Experimental

The method of preparation, physical properties and results of analyses have been published in an earlier communication (*loc.cit.*).

The ultraviolet absorption measurements of *o*-, *m*- and *p*-chloro- and -bromophenyl camphor-*β*-sulphonates (*d*- and *dl*-) were carried out in spectroscopically pure ethyl alcohol and methyl alcohol respectively. The concentrations employed were 0.10% in the case of chloro and 0.05% in the case of bromo esters. The results are recorded in Table I along with the 'characteristic' wave-lengths derived from Drude's *one-term* dispersion equation with a view to comparing them with the absorption maxima obtained by direct measurements.

The rotatory dispersion measurements were carried out in ethyl alcohol, methyl alcohol and chloroform in 2 dcm jacketed tube at 35° in the visible part of the spectrum for 13 wave-lengths from λ=6708 to 4358Å. In the case of *o*-, *m*- and *p* chlorophenyl esters in the three solvents 1 0% solutions were employed for study. In the case of *o*-bromophenyl ester in ethyl alcohol and chloroform and *p*-bromophenyl ester in chloroform, 1.0% solutions were taken whereas 0.5% solutions were used in the cases of *o*-bromophenyl ester in methyl alcohol, *p*-bromophenyl ester in ethyl and methyl alcohols and the *m*-ester in all solvents. The rotatory dispersion measurements are recorded in Tables II and III.

TABLE I

	Camphor-β-sulphonates.	Conc. (g./100 c.c.).	Solvent.	$\lambda_{max.}$	ϵ_{max}	Solvent.	$^{*}\lambda_{\infty}$.	$\lambda_{\infty} - \lambda_{max.}$ (*d*-form).
1.	*o*-Chlorophenyl *d*-	0.10	EtOH	266 mμ 225	319 679	$CHCl_3$ EtOH MeOH	318 345 348	52 & 93 79 & 120 82 & 123
2.	,, *dl*-	0.10	EtOH	266 225	302 679			
3.	*m*-Chlorophenyl *d*-	0.10	EtOH	266 225	360 669	$CHCl_3$ EtOH MeOH	343 293 331	77 & 118 27 & 68 65 & 106
4.	,, *dl*-	0.10	EtOH	266 225	404 689			
5.	*p*-Chlorophenyl *d*-	0.10	EtOH	266 225	330 693	$CHCl_3$ EtOH MeOH	303 320 343	37 & 78 54 & 95 77 & 118
6.	,, *dl*-	0.10	EtOH	266 225	336 710			
7.	*o*-Bromophenyl *d*-	0.05	MeOH	267 228	304 1820	$CHCl_3$ EtOH MeOH	301 330 353	34 & 73 63 & 102 86 & 125
8.	,, *dl*-	0.05	MeOH	267 228	316 1859			
9.	*m*-Bromophenyl *d*-	0.05	MeOH	267 228	357 1820	$CHCl_3$ EtOH MeOH	286 291 308	19 & 58 24 & 63 41 & 80
10.	,, *dl*-	0.05	MeOH	267 228	368 1835			
11.	*p*-Bromophenyl *d*-	0.05	MeOH	267 231	349 1935	$CHCl_3$ EtOH MeOH	323 310 363	56 & 92 43 & 79 96 & 132
12.	,, *dl*-	0.05	MeOH	267 231	321 1936			

* From Drudes one-term equation.

TABLE II

Chlorophenyl d-*camphor-β-sulphonates* (o-, m- *and* p-).

Compound:	*o*-Chlorophenyl-			*m*-Chlorophenyl-			*p*-Chlorophenyl-		
Solvent: Conc. (%): Lines.	$CHCl_3$. 1.00	EtOH. 1.00	MeOH. 1.00	$CHCl_3$. 1.00	EtOH. 1.00	MeOH. 1.00	$CHCl_3$. 1.00	EtOH. 1.00	MeOH. 1.00
6708	27.0	18.0	...	20.5	25.0	19.5	27.5	24.0	17.0
6438	30.0	20.5	17.0	23.5	27.5	22.0	30.5	26.5	19.0
6104	35.0	24.0	19 5	27.0	32.0	25.5	35.0	30.5	22.5
5893	38.5	27.0	22.0	30 0	35.0	28.0	38.5	34 0	25.0
5780	40.5	28 5	23.5	32.0	37.0	30.0	40.5	36.0	26.5
5468	47.5	34.0	28.0	38.0	43.0	35.5	47.5	42.5	32.0
5461	48.0	34.5	28.5	38.5	43.5	36.0	47.5	43 0	32.5
5209	55.5	40.5	33.5	44.5	49.5	42.0	55.0	49.5	37.5
5086	60.0	44.5	37.0	49.0	53.0	45.5	58.5	53.5	41.0
4800	73 0	55.0	46.0	61.0	63.5	56.5	71.0	65.5	51.0
4678	80.0	61.5	51.5	68.0	69.0	62.5	77.5	71.5	57.0
4603	85.5	66.0	55.5	73.0	73.0	66.5	82.0	76.5	61.0
4358	105.0	85.0	72.0	95.0	88.5	84.0	100.0	97.0	77.5

TABLE III

Bromophenyl d-camphor-β-sulphonates (o-, m- & p-).

Compound:	*o*-Bromophenyl-			*m*-Bromophenyl-			*p*-Bromophenyl-		
Solvent:	$CHCl_3$	EtOH.	MeOH.	$CHCl_3$	EtOH.	MeOH.	$CHCl_3$	EtOH.	MeOH.
Conc. (%):	1.00	1.00	0.50	0.50	0.50	0.50	1.00	0.50	0.50
Lines.									
6708	20.0	17.5	15.0	23.0	22.0	20.5	22.5	22.5	13.5
6438	23.5	19.5	17.0	26.0	24.5	23.0	25.0	25.5	15.0
6104	26.5	23.0	20.0	29.5	28.0	26.5	29.0	29.0	18.0
5893	29.0	25.	22.0	32.0	31.0	29.0	31.5	32.0	20.5
5780	31.5	27.0	24.0	34.0	32.5	30.5	34.5	34.0	22.0
5468	36.0	32.0	29.0	39.5	38.0	36.0	40.5	40.0	27.0
5461	36.0	32.5	29.0	9.5	38.0	36.0	40.5	40.0	27.0
5209	41.0	37.5	34.5	45.0	43.5	41.5	47.5	46.0	32.5
5086	44.0	40.0	38.0	48.5	46.5	44.5	51.0	50.0	36.0
4800	53.5	50.0	47.5	57.5	55.5	54.0	62.5	60.0	46.5
4678	58.0	55.0	53.5	62.5	60.5	59.0	69.5	66.0	52.5
4603	62.0	59.0	58.0	65.5	64.0	62.5	74.5	70.0	57.0
4358	75.0	74.5	76.0	79.0	77.0	77.0	92.0	86.0	77.0

DISCUSSION

The ultraviolet absorption of *o*, *m*- and *p*-chlorophenyl camphor-β-sulphonates (*d*- and *dl*-) has been studied in ethyl alcohol and that of *o*-, *m*- and *p*-bromophenyl camphor-β-sulphonates (*d*- and *dl*-) in methyl alcohol, as the absorption spectra are not much modified by change of solvent, the absorption maxima remaining almost the same in different solvents (Singh and Sarma, this *Journal*, 1958, **35**, 463). The esters exhibit two absorption bands, λ_{max_1} at 266 mμ and λ_{max_2} at 225 mμ in the case of chloro esters and λ_{max_1} at 267 mμ and λ_{max_2} at 228 – 231 mμ, in the case of bromo esters; *o*-, *m*- and *p*-isomers (both *d*- and *dl*-) give the same bands excepting *p*-bromophenyl camphor-β-sulphononates (*d*- and *dl*-) which give bands, λ_{max_1} at 267 mμ and λ_{max_2} at 231 mμ, while *o*- and *m*- isomers (*d*- and *dl*) give bands, λ_{max_1} at 267 mμ and λ_{max_2} at 228 mμ (Table I). The molar extinction coefficient, ϵ_{max_1} for the band λ_{max_1} has practically the same value, 302 to 404 for all the esters, both *dextro* and *racemic*. The value of ϵ_{max_2} lies in the range from 669 to 710 in the case of *o*, *m*- and *p*-chlorophenyl esters (*d*- and *dl*-) and from 1820 to 1936 in the case of *o*-, *m*- and *p*-bromophenyl esters (*d*- and *dl*-), as shown in Table I.

The rotatory dispersion of *o*-, *m*- and *p*-chlorophenyl and *o*-, *m*- and *p*-bromophenyl camphor-β-sulphonates (*d*- and *dl*-) in three solvents, chloroform, ethyl alcohol and methyl alcohol, can be expressed by Drude's one-term equation :

$$[\alpha]_\lambda = \frac{K}{\lambda^2 - \lambda_o^2}$$

within experimental limits. It can also be expressed by Drude's two-term equation :

$$[\alpha]_\lambda = \frac{K_1}{\lambda^2 - \lambda_1^2} + \frac{K_2}{\lambda^2 - \lambda_2^2}$$

with λ_{max_1} and λ_{max_2} used for λ_1 and λ_2 in the equation ; the agreement between the calculated and the observed values of rotation is as good as in the case of one-term equation. The various one-term and two-term equations, derived to express the observed rotatory dispersion of the esters in different solvents, are shown in Tables IV and V respectively.

TABLE IV

One-term equations derived for chloro- and bromophenyl d-camphor-β-sulphonates.

Esters of *d*-camphor-β-sulphonic acid.	$CHCl_3$.	EtOH.	MeOH.
o-Chlorophenyl	$\frac{9.418}{\lambda^2-0.1012}$ (3181 Å)*	$\frac{6.065}{\lambda^2-0.1187}$ (3445 Å)	$\frac{4.980}{\lambda^2-0.1208}$ (3475 Å)
m-Chlorophenyl	$\frac{6.898}{\lambda^2-0.1173}$ (3426Å)	$\frac{9.176}{\lambda^2-0.0861}$ (2934Å)	$\frac{6.725}{\lambda^2-0.1099}$ (3314 Å)
p-Chlorophenyl	$\frac{9.827}{\lambda^2-0.0917}$ (3028Å)	$\frac{8.353}{\lambda^2-0.1021}$ (3196Å)	$\frac{5.729}{\lambda^2-0.1179}$ (3434Å)
o-Bromophenyl	$\frac{7.496}{\lambda^2-0.0906}$ (3010Å)	$\frac{6.072}{\lambda^2-0.1085}$ (3295Å)	$\frac{4.954}{\lambda^2-0.1248}$ (3533Å)
m-Bromophenyl	$\frac{8.548}{\lambda^2-0.0818}$ (2861Å)	$\frac{8.118}{\lambda^2-0.0846}$ (2909Å)	$\frac{7.315}{\lambda^2-0.0950}$ (3082Å)
p-Bromophenyl	$\frac{7.607}{\lambda^2-0.1045}$ (3232Å)	$\frac{8.086}{\lambda^2-0.0960}$ (3098Å)	$\frac{4.497}{\lambda^2-0.1316}$ (3627Å)

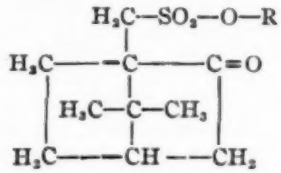
* The values of λ_a are shown in parenthesis.

TABLE V

Two-term equations derived for chloro- and bromophenyl d-camphor-β-sulphonates.

d-Camphor-β-sulphonate.	$CHCl_3$.	EtOH.	MeOH.
o-Chlorophenyl	$\frac{32.350}{\lambda^2-0.0708} - \frac{23.284}{\lambda^2-0.0506}$	$\frac{39.790}{\lambda^2-0.0708} - \frac{34.660}{\lambda^2-0.0506}$	$\frac{36.564}{\lambda^2-0.0708} - \frac{32.702}{\lambda^2-0.0506}$
m-Chlorophenyl	$\frac{41.034}{\lambda^2-0.0708} - \frac{35.124}{\lambda^2-0.0506}$	$\frac{19.284}{\lambda^2-0.0708} - \frac{10.271}{\lambda^2-0.0506}$	$\frac{34.672}{\lambda^2-0.0708} - \frac{28.818}{\lambda^2-0.0506}$
p-Chlorophenyl	$\frac{26.163}{\lambda^2-0.0708} - \frac{16.643}{\lambda^2-0.0506}$	$\frac{32.856}{\lambda^2-0.0708} - \frac{28.163}{\lambda^2-0.0506}$	$\frac{34.061}{\lambda^2-0.0708} - \frac{29.091}{\lambda^2-0.0506}$
o-Bromophenyl	$\frac{18.376}{\lambda^2-0.0713} - \frac{11.061}{\lambda^2-0.0520}$	$\frac{29.538}{\lambda^2-0.0713} - \frac{24.060}{\lambda^2-0.0520}$	$\frac{41.401}{\lambda^2-0.0713} - \frac{37.644}{\lambda^2-0.0520}$
m-Bromophenyl	$\frac{15.188}{\lambda^2-0.0713} - \frac{6.756}{\lambda^2-0.0520}$	$\frac{16.392}{\lambda^2-0.0713} - \frac{8.431}{\lambda^2-0.0520}$	$\frac{22.746}{\lambda^2-0.0713} - \frac{15.818}{\lambda^2-0.0520}$
p-Bromophenyl	$\frac{36.896}{\lambda^2-0.0713} - \frac{29.819}{\lambda^2-0.0534}$	$\frac{27.199}{\lambda^2-0.0713} - \frac{19.553}{\lambda^2-0.0534}$	$\frac{54.362}{\lambda^2-0.0713} - \frac{52.042}{\lambda^2-0.0534}$

The rotatory dispersion of camphor is complex and can be expressed by Drude's two-term equation containing the low frequency pertaining to the selective absorption band (λ_{max} 2880Å) of camphor which is characteristic of the unsaturated ketonic group, $>C=O$ (Lowry and French, *J. Chem. Soc.*, 1924, **125**, 1923). The ketonic group which is responsible for the complex rotation of camphor is left intact in the esters of camphor-β-sulphonic acid with the structure :



It is therefore probable that the same ketonic group would give rise to complex rotation in the case of the esters of camphor-β-sulphonic acid. The 'characteristic' wave-lengths in Drude's equation :

$$[\alpha]_\lambda = \sum \frac{K_n}{\lambda^2 - \lambda_n^2}$$

corresponding to the frequencies of the classical electronic oscillators governing rotation, therefore, should also correspond to the absorption maxima of the compound. But the values of λ_os derived from Drude's one-term equation differ very much from those of λ_{max} obtained by direct measurement. When the two absorption maxima, λ_{max_1} and λ_{max_2} are substituted in the place of λ_1 and λ_2, the 'characteristic' wave-lengths in Drude's two-term equation, not only does the equation represent the observed rotation quite precisely, but also affords a fully physical significance to the equation.

The authors express their gratefu thanks to Dr. Bawa Kartar Singh, Retired Hony. Professor and Head of the Organic Chemistry Research Section, for suggesting the problem and initiating them into the investigation, and also to the Banaras Hindu University for the research facilities and the award of a Research Assistantship to one of them (S.R. Sarma).

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A STUDY OF THE ALKALINE HYDROLYSIS OF CHLOROFORM IN ETHYL ALCOHOL SOLUTION

By Sameer Bose

Carbon monoxide, ethylene and formic acid, produced on treating chloroform with alcoholic potassium hydroxide, have been estimated. The precision is 5% for gas analysis and 1% for formate estimation. Under suitable conditions 60% of the gas evolved is ethylene. The reaction was carried out in a Lunge nitrometer under varying conditions of temperature and concentration of the reactants. Formic acid and carbon monoxide produced have been correlated with the chloroform decomposed. Analytical evidence has been adduced in support of the view that ethylene arising from the reaction is formed from ethyl alcohol. Probable mechanism of its formation through the intermediacy of carbon dichloride has been discussed.

Several workers attempted to elucidate the mechanism of the alkaline hydrolysis of chloroform, but failed to reach a definite conclusion. Saunders (*J. Phys. Chem.*, 1900, **4**, 660) found that the rate of hydrolysis of chloroform by alkali in 95% ethyl alcohol was of the first order with respect to both hydroxide and chloroform concentrations. Abel (*Z. Elektrochem.*, 1923 **29**, 391) reported that in very dilute solutions the reaction was of the first order, being independent of alkali concentration, but with increase in alkali concentration the order was found to increase. Hine (*J. Amer. Chem. Soc.*, 1950, **72**, 2438), using aqueous dioxane solutions, found the reaction to be bimolecular. This divergence in the kinetic order is probably due to variation in the products as well as in the mechanism of the reaction with temperature and concentration of the reactants. In the present work a comprehensive quantitative analysis of the reaction products has been undertaken using a Lunge nitrometer as the reaction vessel which facilitates the analysis of the gaseous products. The evolution of carbon monoxide in this reaction was first noticed by Hermann (*Annalen*, 1855, **95**, 211) and later by Geuther (*ibid.*, 1862, **123**, 121). Bassett (*ibid.*, 1864, **132**, 54) reported that the gas produced by the reaction of sodium ethoxide with chloroform was inflammable; he presumed it to be a mixture of carbon monoxide and ethylene. Mossler (*Monatsh.*, 1903, **29**, 373) found that the reaction yielded a gaseous mixture of 25% ethylene and 75% carbon monoxide whether the ethyl alcohol was absolute or mixed with water and whether the chloroform or alkali was in excess. In contradiction to the observations of Mossler it was found that the quantity and the composition of the gas evolved, as well as the amount of formate formed, varied with the temperature and concentration of the reactants. When chloroform was in excess, the volume of the gas evolved increased and the formate formed diminished, while an opposite effect was afforded by excess of alkali. Hermann (*loc. cit.*) regarded the formation of ethylene due to dehydration of the solvent (ethyl alcohol), a view which was supported by Hine *et al.* (*J. Amer. Chem. Soc.*, 1953, **75**, 5607) and the present work. Nef (*Annalen*, 1897, **298**, 367) has, however, stated that the reaction of bromoform and

alkali involves a dissociation of bromoform to Br_2 and CHBr, dimerisation of the latter and reduction of $C_2H_2Br_2$ to ethylene. The evolution of a large amount of ethylene from a comparativety small amount of chloroform makes Nef's mechanism improbable.

EXPERIMENTAL

Procedure.—Standard solutions of chloroform and alkali were pipetted into a 50 c.c. Lunge nitrometer (filled with mercury), using 1 c.c. of alcohol for washing the cup of the nitrometer. The solutions were thoroughly mixed by shaking the nitrometer, all the air in it was driven out and the mercury level adjusted to the zero mark. The heating was carried out by immersing the nitrometer along with its levelling tube in a tall thermostat ($2' \times 1' \times \frac{3}{4}'$) maintained at a suitable temperature ($\pm 0.5°$). Vigorous reaction took place with rapid evolution of gases, specially when the bath was above 60°. The heating was continued till the reaction was over; an additional 15 minutes' heating was done to ensure completion of the reaction. Whenever the solvent developed a tendency to boil, the gas pressure in the nitrometer was increased by raising the levelling tube considerably. After the reaction was over, the nitrometer was cooled and the gases were transferred to a 50 c.c. mercury-filled Hempel burette. A part of the gas was found to dissolve in the alcohol; this was extracted repeatedly under low pressure after heating the solvent to about 60°. The reaction mixture remaining in the nitrometer was extracted with hot water and the volume made up to 100 c.c. Crystals of potassium chloride were found to stick to the walls of the nitrometer below the mercury level; these were removed by flushing the whole of the nitrometer with hot water.

Method of Analysis.—Potassium chloride was estimated in 25 c.c. of the above aqueous solution after acidifying with nitric acid, followed by titration according to Volhard.

A modification (Bose, this *Journal*, 1958, **35**, 320) of Fuchs' method (*Z. anal. Chem.*, 1929, **78**, 125) involving oxidation by mercuric chloride ($2HgCl_2 + HCOOK = Hg_2Cl_2 + KCl + HCl + CO_2$) was used for evaluating the formate ion. The aqueous solution (70 c.c.) was taken in a 250 c.c. pyrex flask and evaporated to dryness on a water-bath after titrating the hydroxide content with 0·1*N*-H_2SO_4 to phenolphthalein end-point. The residue was redissolved in a little water and then taken up for the formate estimation. The gravimetric (472 mg. calomel ≡46 mg. HCOOH) and the volumetric results, obtained by titrating the hydrochloric acid liberated, were found to agree with a precision of 1%. The results for formic acid recorded in this paper represent the average of the volumetric and gravimetric determinations.

The gases produced were collected in a Hempel burette and analysed by two different methods. Ethylene in the first method (Francis *et al.*, *Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 703) was absorbed in a 20% solution of mercuric sulphate in 25% H_2SO_4, while in the second method (Imperial Chem. Industries, G. P. 548, 872/1928; *Chem. Abs.*, 1932, **26**, 4114) which appeared to be more elegant, 0·2*N*-HNO_3 containing 50% silver nitrate was used. Ethylene alone was taken up by

both the solutions, leaving carbon monoxide unabsorbed. The two methods provided identical results for ethylene. Carbon monoxide was absorbed in an acidified solution of cuprous chloride. In the first method, where mercuric sulphate was used for absorbing ethylene, a part of the carbon monoxide was oxidised to CO_2 (Brooks *et al.*, *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 339) and therefore could not be completely absorbed in cuprous chloride solution. All absorbents were taken in 25 c.c. Hempel pipettes and were allowed to act till no further absorption took place.

(*a*). *Effect of Temperature.*—The total volume of gas evolved showed a temperature dependence. It increased with rise in temperature, while the formate produced decreased. 1.52*N*-KOH solution (5 c.c.) was made to react with 2 c.c. of 0.49*M* chloroform solution at different temperatures. An analysis of the products is recorded in Table I. Assuming that chloroform decomposed to furnish formic acid and carbon monoxide, the values for potassium formate were calculated by deducting molecules of carbon monoxide evolved from the total number of molecules of chloroform decomposed. The fact that the calculated and the experimental values are in fair agreement, bears out the above assumption. As all the carbon atoms in chloroform can be accounted for in CO and HCOOK, the only conclusion that can be drawn with regard to the origin of ethylene is that, it is formed from ethyl alcohol.

TABLE I

Effect of temperature in presence of excess of KOH.

(7.6 m*M* of KOH + 0.97 m*M* of $CHCl_3$ in 8 c.c. EtOH).

Temp.	Heating time.	Millimoles (×10) of KOH used.	KCl formed.	Pot. formate. Expt.	Pot. formate. Calc.	CO (at N.T.P.).	C_2H_4 (at N.T.P.).
25°	100 hrs.	38.6	29.2	9.3	9.2	0.8 c.c.	1.2 c.c.
40°	20	38.0	29.0	9.0	9.1	1.3	1.2
60°	5	38.3	29.3	9.2	9.0	1.5	1.5
70°	3	37.9	29.2	8.6	8.8	2.0	2.5
80°	1	37.8	29.1	8.5	8.4	2.6	4.6
90°	½	36.9	29.0	7.6	7.9	4.0	6.2

(*b*). *Effect of excess of either of the Reagents.*—Keeping temperature the same (80°), the chloroform and the hydroxide concentrations were altered. Gas evolution was found to increase with the use of excess of chloroform. Experiments were carried out in which the hydroxide concentration was kept the same and that of chloroform gradually increased (Table II, expts. 1 to 5). A diminution in the volume of gas was observed when chloroform concentration was kept the same and that of alkali gradually increased (Table II, expts. 5 to 9).

TABLE II

Effect of adding excess of reagent at 80°.

(Amount of $CHCl_3$ decomposed is practically the same in all the expts.).

Expt. No.	Excess of reagent used.	Millimoles (×10) of KOH consumed.	KCl formed.	Pot. formate Expt.	Pot. formate Calc.	CO (at N.T.P.).	C_2H_4
1.	$CHCl_3$ (600%)	35.6	30.2	5.3	5.4'	10 3 c.c.	6.5 c.c.
2.	,, (300%)	36.2	30.0	6.3	6.1	8.6	6.0
3.	,, (150%)	36.3	30.2	6.2	6.4	8.2	4.8
4.	,, (10%)	36.9	29.8	7.0	6.9	6.5	3.5
5.	Stoichiometric proportions	37.0	29.5	7.2	7.2	5.7	2.9
6.	KOH (10%)	37.6	30 0	7.5	7.7	5.0	4.0
7.	,, (50%)	38.3	30.1	8.3	8.1	4.1	3.7
8.	,, (100%)	38.5	30.0	8.5	8.6	3 0	2.6
9.	,, (400%)	38.6	29.5	8.8	9.1	1.6	1.4

(*c*). *Effect of Dilution*.—The two reactants were taken in stoichiometric proportions and diluted with varying quantities of ethyl alcohol. The evolution of gas diminished, while the amount of formate produced increased with dilution. Strangely enough, an opposite effect was produced when water was used as the diluent, as shown in Table III.

TABLE III

Effect of dilution at 80°.

(Reagents present in stoichiometric proportions in 8 c.c. EtOH).

Expt. No.	Diluent used.	Millimoles (×10) of KOH consumed.	KCl formed.	Pot formate Expt.	Pot formate Calc.	CO (at N T.P.)	C_2H_4
1.	Water 20 c.c.	35.3	29.3	5.8	6.0	8.0	9.1 c.c.
2.	,, 15	35.0	29.2	6.1	6.2	7.7	8.1
3.	,, 10	35.6	29.2	6.2	6.5	7.0	7.0
4.	,, 5	36.1	29.0	7.2	7.4	6 0	6.5
5.	Nil	36.1	29.1	6.9	7.2	5.4	4.4
6.	EtOH 5	37.3	29.3	7.8	7.8	4.1	3.2
7.	,, 10	37.2	29.0	8.4	8.2	3.3	2.0
8.	,, 15	37.6	29.0	8.7	8.8	2.1	1.7
9.	,, 20	38.1	29.1	9.3	9.2	1.0	2.0

DISCUSSION

A mixture of chloroform and potassium hydrxoide possesses a strong reducing power which cannot be accounted for by the mere presence of formate ion. This Vorländer *et al.* (*Ber.*, 1929, **62B**, 549) explained by postulating the formation of an active isomer of carbon monoxide or hydroxyformaldehyde as an intermediate compound. Although it is probable that an active isomer of carbon monoxide is produced, but the evidences put up by Vorländer in its favour are meagre. Hine (*loc. cit.*) has put up a strong case in favour of formation of carbon dichloride

during the basic hydrolysis of chloroform in aqueous dioxane solution. He has suggested the following mechanism :

$$CHCl_3 + OH^- \overset{\text{Fast}}{\rightleftharpoons} CCl_3^- + H_2O$$

$$CCl_3^- \xrightarrow{\text{Slow}} Cl^- + CCl_2$$

$$CCl_2 \xrightarrow[H_2O]{OH^- \text{ fast}} CO + HCOO^-$$

He has stated "... if carbon dichloride is a highly reactive intermediate, as it may well be expected to be, its great reactivity should tend to favour reaction with the reagent present in the greatest concentrations". He was, however, working with dioxane solutions, but in the present experiments ethyl alcohol was present in large concentrations. It is very probable that the carbon dichloride produced not only undergoes hydrolysis but also undergoes alcoholysis. The following is the probable mechanism leading to the formation of ethylene from ethyl alcohol (analytical proof already adduced) :

$$CCl_2 + 2\,EtOH \longrightarrow 2EtCl + C(OH)_2$$

$$EtCl + KOH \longrightarrow KCl + H_2O + C_2H_4$$

$$C(OH)_2 \longrightarrow CO + H_2O$$

$$C(OH)_2 \longrightarrow HCOOH$$

The direct alcoholysis of chloroform was found to be a very slow process even at 80°. After heating an alcoholic solution of chloroform (0.2*M*) for an hour at 80° in the Lunge nitrometer, an attempt was made to extract the ethyl chloride (if produced) under vacuum at 40°, but no gas could be collected. In conclusion it may be stated that chloroform molecules on hydrolysis decompose to afford quantitatively carbon monoxide and formic acid. The fact that the calculated values of formic acid agree with the experimental ones, proves the above contention.

The author wishes to thank sincerely the authorities of the college, specially Principal Uma Das Mukerji, for provding all the facilities needed for this work.

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CHEMISTRY OF DIFLUOROARSENATES. PART I. DIFLUOROARSENIC ACID AND DIFLUOROARSENATES OF ALKALI METALS

By Asim Bikash Ray and Grihapati Mitra

Difluoroarsenic acid and the difluoroarsenates of ammonium and alkali metals have been prepared and their properties studied. Difluoroarsenic acid boils with decomposition and attacks the filter paper. It cannot be stored in glass bottles as it corrodes the glass. Lithium difluoroarsenate crystallises with three molecules of water while the corresponding sodium salt does with one. Potassium and rubidium difluoroarsenates are found to be sparingly soluble in water. Silver difluoroarsenate possibly exists in solution.

Two oxyfluorides of pentavalent phosphorus are well known (Lange, "Fluorine Chemistry", edited by J. H. Simmons, pp. 126-189). The corresponding anions of pentavalent arsenic, e.g., monofluoarsenate, AsO_3F^{2-} and difluoroarsenates $AsO_2F_2^-$, are not found in the literature. The monofluoroarsenates have been isolated recently (A.B. Ray, D.Sc. thesis, Calcutta University, 1955 ; Dutt and Gupta, *Z. anorg. alleg. Chem.*, 1956, **235**, 92).

The difluoroarsenate ion may be represented in keeping with the structure of the corresponding phosphorus ion as :

Phosphates and arsenates behave similarly and some of the phosphates have been proved to be isomorphous with the corresponding arsenates (Helmholz and Levine, *J. Amer. Chem. Soc.*, 1942, **64**, 354). The oxyfluoride anions of arsenic, however, are larger than the corresponding oxyfluoride anions of pentavalent phosphorus (Chakravarty, Ray and Mitra, unpublished work). The X-F distances in PF_3 and AsF_3 are 1.52Å and 1.72Å respectively (Gregg *et al.*, *Trans. Faraday Soc.*, 1937, **33**, 852). Pauling ("The Nature of Chemical Bond", p. 235) has also attributed some double bond character in PF_3.

The chemistry of the difluoroarsenic acid and the salts of alkali metals and ammonia is being discussed in the present communication. As expected, the difluoroarsenates exhibit some resemblance with the corresponding difluorophosphates, and therefore with the corresponding perchlorates, but as the anions are smaller in the latter cases, the difluoroarsenates are found not to be isomorphous with the corresponding difluorophosphates.

EXPERIMENTAL

Arsenic was estimated as the trisulphide after reduction with SO_2. For flourine the compound was treated with an excess of $AgNO_3$ solution in neutral medium when Ag_3AsO_4 was precipitated. The solution after filtration was treated with NaCl solution when the excess of silver was removed as the chloride. After washing the precipitate, fluorine was estimated as CaF_2. The alkali metals were estimated as sulphate after removal of arsenic as sulphide.

Difluoroarsenic acid was obtained by digestimg on the water-bath calculated amounts of arsenic pentoxide and hydrofluoric acid according to:

$$As_2O_5 + 4HF = 2HAsO_2F_2 + H_2O.$$

A weighed amount of arsenic trioxide was taken in a platinum basin and was oxidised to As_2O_5 by HNO_3 (conc.), the excess of which was removed by evaporating it to dryness. To this solid pentoxide, left in the basin, a slightly greater amount of HF than that required theoretically was added. The mixture was digested on the water-bath for about 1½ hours when a viscous liquid was left, which was analysed. (Found: As, 30.23; F, 15.89. Calc. for $HAsO_2F_2, 5H_2O$: As, 31.79; F, 16.10%).

The percentages of As and F remained approximately constant at this temperature (85-90°). A little more hydrofluoric acid was added to this acid and this was once again allowed to evaporate for 1½ hours. The viscous liquid on analysis showed approximately the same percentages of As and F. This showed that the liquid left in the basin was difluoroarsenic acid. Difluoroarsenic acid was found to be corrosive and attacked filter paper. It also attacks glass slowly and decomposes before boiling even at 10 mm pressure.

Ammonium Difluoroarsenate.—A weighed amount of arsenic trioxide was oxidisied by HNO_3 (conc.) to the pentoxide. The excess of the acid was removed by evaporation on an asbestos board. A saturated solution of the calculated amount of ammonium bifluoride was made in a platinum basin. To this solution As_2O_5 was gradually added while the mixture was warmed on a water-bath. After the addition of the pentoxide was completed, HNO_3 (conc., 0.5-1 c.c.) was added to the mixture dropwise; the mixture was digested on the water-bath to completion (1 hr.), cooled, filtered and allowed to crystallise in a vacuum desiccator (H_2SO_4). After a few days colorless crystals appeared. These were filtered under suction, washed with 60% alcohol and analysed (Found: N, 8.52; As, 45.96; F, 23.00. $NH_4AsO_2F_2$ requires N, 8.58; As, 45.98; F, 23.23%). It may be noted that in absence of nitric acid an impure product containing arsenate is obtained.

$$As_2O_5 + 2NH_4HF_2 = 2NH_4AsO_2F_2 + H_2O.$$

Ammonium difluoroarsenate is highly soluble in water. The concentrated solution did not form any precipitate with barium chloride or calcium chloride solution in the cold. The latter, however, afforded a precipitate on long standing or on warming. The data obtained from the powder picture are recorded in Table I.

TABLE I

d.	Intensity.	*d.*	Intensity.	*d.*	Intensity.	*d.*	Intensity.	*d.*	Intensity.
4.98Å	S.	2.05Å	S.	1.56Å	MW.	1.28Å	MW.	1.04Å	M
3.94	MS.	1.90	W.	1.50	MS.	1.24	M.	0.97	MW.
3.13	VS.	1.80	M.	1.39	M.	1.21	W.	0.94	VW.
2.70	MW.	1.71	M.	1.35	MW.	1.81	W.	0.93	W.
2.41	W.	1.63	M.	1.31	MW.	1.06	W.	0.92	W.

VS = very strong ; S = strong ; MS = medium strong ; M = medium ; MW = medium weak and W = weak.

These spacings on comparison with the standard spacings of ammonium perchlorate are not found to be isomorphous. This compound, however, resembles ammonium dihydrogen phosphate very closely. Further investigations are required to prove the isomorphism of this compound with $NH_4H_2PO_4$

Lithium difluoroarsenate was obtained by digesting on the water-bath a mixture containing the calculated amounts of lithium fluoride, arsenic pentoxide and hydrofluoric acid according to the equation :

$$2LiF + As_2O_5 + 2HF = 2Li\,AsO_2F_2 + H_2O.$$

The method of procedure was exactly the same as described before. The compound was washed with 60% alcohol and analysed after drying. (Found : Li, 3.16; As, 36.32 ; F, 18.23. $LiAsO_2F_2,3H_2O$ requires Li, 3.37 ; As, 36.39 ; F, 18.46%).

These beautiful crystals are soluble in water, but in contrast to the perchlorate are sparingly soluble in alcohol. It is of interest to note in this connection that lithium perchlorate also crystallises with three molecules of water.

Sodium difluoroarsenate was prepared in the way as the preceding lithium compound. The colorless crystals were analysed. (Found : As, 40.26 ; F, 20.20. $NaAsO_2F_2,H_2O$ requires As, 40.29 ; F, 20.44%).

The compouud is highly soluble in water and is slightly deliquescent. It may be mentioned here that sodium perchlorate also crystallises with one molecule of water.

Potassium difluoroarsenate was obtained by the following three ways :

(*i*). Starting from KHF_2 and As_2O_5, it was obtained in the same way as described under ammonium difluoroarsenate.

(*ii*). By the addition of potassium nitrate solution to difluoroarsenic acid.

(*iii*). A mixture of the concentrated solutions of potassium nitrate and ammonium difluoroarsenate was warmed on a water-bath for about 15 minutes, cooled to room temperature, and allowed to stand for some time when a gelatinous precipitate was obtained, which was recrystallised from hot water. (Found : K, 21.00, 21.08, 21.03 ; As, 40.50, 40.68, 40.48 ; F, 20.40, 20.68, 20.52. $KAsO_2F_2$ requires K, 21.24 ; As, 40.71 ; F, 20.65%).

Potassium difluoroarsenate is sparingly soluble in water.

Rubidium Difluoroarsenate.—On warming on a water-bath a mixture of concentrated solutions of ammonium difluoroarsenate and rubidium chloride for about 20 minutes and subsequent cooling, a white precipitate was obtained. This was filtered under suction and washed with water till free of ammonium salts. The product was then recrystallised from boiling water, washed as usual, dried and analysed. (Found: As, 32.31; F, 16.44. $RbAsO_2F_2$ requires As, 32.51%; F, 16.49%). This white crystalline substance is sparingly soluble in water.

Silver Difluoroarsenate.—Attempts were also made to isolate the difluoroarsenate of silver by digesting in a platinum basin the requisite quantities of silver flouride, arsenic pentoxide and hydrofluoric acid. A clear solution was obtained which was concentrated in a vacuum desiccator. After a few days chocolate-coloured silver arsenate and a colorless needle-shaped crystalline substance were obtained. The latter could not be obtained in a pure form as silver arsenate was always present as an impurity. Addition of water to these crystals resulted in the precipitation of a greater amount of silver arsenate; the filtrate was found to contain fluoride ions. As the addition of potassium nitrate to the mother-liquor resulted in the precipitation of potassium difluoroarsenate, it appeared that the solution after concentration contained silver difluoroarsenate.

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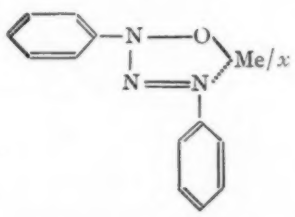
PREPARATION AND STUDY OF HYDROXYTRIAZENES* AS ANALYTICAL REAGENTS. PART I

By N. C. Sogani and S. C. Bhattacharyya

Hydroxytriazenes, possessing the functional grouping -N(OH)-N=N-, introduce a new and interesting complex-forming group, having considerable scope for further research. A general method of preparation of these compounds has been described along with their physical and chemical properties, general precipitating characteristics, *p*H range for complete precipitation with various elements, and the nature of the colour of the complexes formed.

Recently Sogani and Bhattacharyya (*Anal. Chem.*, 1956, **28**, 81, 1616) have reported the use of 3-hydroxy-1 : 3-diphenyltriazene as a highly selective reagent for the gravimetric estimation of palladium and copper. In reproducibility of results, specificity and stability of the metal complexes towards heat and acid, the reagent has been claimed by the authors to be a definite improvement in the class of compounds belonging to Cupferron group (ammonium salt of nitrosophenylhydroxylamine). Different substituents in the 'phenylazo moiety' of the above compound provided very interesting results. Thus, 3-hydroxy-1-*p*-chlorophenyl-3-phenyltriazene precipitated titanium quantitatively as a bright, orange-coloured complex (*loc. cit.*). The sulphonic acid derivative, 3-hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazene has been found to be an excellent colorimetric reagent for palladium (*ibid.*, 1957, **29**, 397) and molybdenum (unpublished). The general structure of the complexes is as follows :



This class of compounds introduces a very interesting and useful complex-forming group, having considerable scope for further development. These can be prepared easily from common laboratory chemicals and are stable towards heat, light and air. The complexes formed by them are often directly weighable and are stable towards heat and mineral acids of moderate concentrations. In the present communication, the general method of preparing these compounds, their physical and chemical properties, general precipitating characteristics, *p*H range for complete precipitation of various elements and the nature and the colour of the complexes formed have been described.

* In the present communication the expression 'hydroxytriazene' has been used instead of 'hydroxytriazine', as in previous publications (Authors).

EXPERIMENTAL

Bamberger (*Ber.*, 1896, **29**, 104; 1897, **30**, 2280; 1899, **32**, 1677; 1900, **33**, 3510) and Gebhard and Thomson (*J. Chem. Soc.*, 1909, **95**, 771, 774, 776) have described the preparation of hydroxytriazenes by reducing nitrobenzene or substituted nitrobenzene with phenylhydrazine or substituted phenylhydrazine. In the present investigation these compounds have been prepared by the reaction of phenylhydroxylamine and diazonium salt in acetate-buffered solution at 0°. The general mechanism of the reaction is as follows:

$$Ph.NH-OH + Ph.N=N.Cl \longrightarrow Ph.N(N=N.Ph)-OH + HCl$$

The preparation of the parent compound, 3-hydroxy-1:3-diphenyltriazene, has been already described by us (*loc. cit.*). The general method of preparing these compounds is described below.

An aqueous-alcoholic solution of freshly prepared phenylhydroxylamine was stirred mechanically with a sufficient quantity of crushed ice to keep the temperature at 0°. A solution of benzenediazonium chloride or substituted benzenediazonium chloride, in molar proportions, was then added slowly to the above solution under mechanical stirring. Small portions of a concentrated solution of sodium acetate were added occasionally to prevent the solution from becoming too acidic and to maintain the *p*H at about 5.0. The required triazene derivative was generally thrown down in the form of a granular precipitate. It was filtered under suction and crystallised from alcohol or acetone or the mixture of the two, as the case required. Table I summarises the physical properties of the compounds prepared.

TABLE I

Compound. $C_6H_5N(OH)N=N-R$ where R− =	Cryst. from.	M. P.	Cryst. appearance.	% Nitrogen. Found.	Calc.
1. $-C_6H_5$	95% Alcohol	119.5°	Pale yellow needles	20.16	19.90
2. $-C_6H_4Cl$ (*p*)	Do	140°	Light greenish yellow needles	17.08	16.97
3. $-C_6H_4Cl$ (*o*)	Do	78.5°	Light green needles	17.37	16.97
4. $-C_6H_4COOH$ (*p*)	1:1-Alc.-acetone	184°	Pale yellow, fluffy	15 61	15.28
5. $-C_6H_4NO_2$ (*p*)	Acetone, large vol.	157°	Deep yellow, fluffy	22.04	21.70
6. $-C_6H_4SO_3Na$, H_2O	Alcohol, large volume	157°	Light green needles	12.42	12.32

A characteristic property of all these compounds is that these hydrolyse on heating in weakly acidic medium. Thus, 3-hydroxy-1:3-diphenyltriazene initially hydrolyses to phenylhydroxylamine and diazonium salt, which are subsequently converted into water-soluble products, *p*-aminophenol and phenol respectively.

These compounds in alkaline medium develop an intense yellow colour. This probably involves a tautomerisation of the compound according to the equation:

$$\text{Ph.}\ \underset{\underset{\text{N=N.Ph}}{|}}{\text{N-OH}} \rightleftharpoons \underset{\underset{\text{N-NH.Ph}}{\|}}{\text{Ph.N=O}}$$

All the compounds showed absorption peak at 350 mμ, which is possibly due to the presence of 'azo' group (Brode, "Chemical Spectroscopy", J. Wiley & Sons, N. Y., 1943). Substitution of chloro, sulphonic or carboxylic groups in the parent compound does not make any appreciable change in the spectral characteristics. A Beckman quartz spectrophotometer, model DU, was used in this investigation.

Reactions with Various Elements

The reactions were carried out by adopting conventional procedures using spot plate, micro test-tubes, hand centrifuge etc. *p*H was determined by using *p*H paper and also a Beckman *p*H meter, model H-2.

The reactions shown by the parent compound, 3-hydroxy-1 : 3-diphenyltriazene, towards various elements were studied thoroughly. 1% Solution of the reagent in 95% ethyl alcohol was added dropwise to 0.5 c.c. of 1% metallic ion solution taken in a series of test tubes. *p*H was adjusted by adding *N*-HCl and 10% sodium acetate solution. The formation of any precipitate or colour change in the mixture was noted both in the cold and on heating. In case where there was any precipitate, its formation was completed by further addition of the reagent and warming the mixture on a water-bath. Completeness of the precipitation was tested by applying the spot test on the filtrate. The results are recorded in Table II.

TABLE II

Reactions of 3-hydroxy-1 : 3-diphenyltriazene with various elements.
[N. Q. denotes not quantitative].

Elements.	*p*H for quantitative pptn.	*p*H, below which there is no reaction.	Colour of the complex.	Remark.
Cu^{2+}	1.9 to 7.0	...	Chocolate brown	Granular, stable towards heat.
Ni^{2+}	4.4 to 7.0	3.5	Bright yellow	Granular, stable towards heat.
Co^{2+}	5.0 to 7.0	4.0	Dark brown	Granular, slightly soluble in water.
Mn^{2+}	N. Q.	5.5	Dirty brown	Unstable towards heat.
Cd^{2+}, Zn^{2+}	N. Q.	6.0	Light yellow	Fine precipitate.
Pb^{2+}	N. Q.	7.5	Light yellow	Fine precipitate.
Fe^{2+}, Fe^{3+}	4.5 to 7.0	Up to low *p*H	Bluish black	Granular, unstable towards heat.
Sn^{2+}, Sn^{4+}	N. Q.	6.5	Yellow	Fine ppt., partial pptn.
Hg^{2+}	4.5 to 7.0	4.0	Yellow	Fine, unstable towards heat.
Pd^{2+}	1.6 to 7.0	...	Yellowish brown	Granular, stable towards heat.
Ti^{4+}	2.0 to 3.5 (at low *p*H only)	...	Orange	Unstable towards heat, fairly soluble in alcohol.
V^{4+}	,, ,,	...	Grassy green	Unstable towards heat, fairly soluble in alcohol.
Vanadate	,, ,,	...	Dark green	Do
Molybdate	,, ,,	...	Deep orange-red	Do
Ag^{+}, Au^{3+}, Os^{4+}	...	...	...	Reduced to the metallic state.

As^{3+}, Sb^{3+}, Bi^{3+}, Al^{3+}, Be^{2+}, Cr^{3+}, Th^{4+}, Ge^{4+}, Ce^{4+}, U^{4+}, UO_2^{2+}, Zr^{4+}, ZrO_2^{2+}, Pt^{4+}, Ru^{4+}, Ru^{3+}, Ir^{3+}, alkali and alkaline earth metals, tungstate, phosphate, borate, fluoride, oxalate and other anions gave no reaction with the reagent. The reactions were completely masked by cyanide.

The results are also, more or less, true of other members of the triazene series, so far as the specificity, *p*H limit and colour of the complexes are concerned. The precipitates formed by the *p*-chloro derivative were more stable as compared to the complexes formed by the parent reagent. Precipitates formed by the *o*-chloro derivative were gelatinous in nature and were unstable towards heat. This is presumably due to the steric hindrance created by the *ortho*-substitution which prevents the formation of stable complexes. The complexes formed by the *p*-carboxy derivative were also gelatinous in nature and not useful for analytical purposes. The nitro compound and its complexes were particularly insoluble. The colour intensities of these complexes were more than those formed by other compounds. The complexes formed by the sulphonic acid derivative were, like the reagent itself, soluble in water.

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GUANYLALKYLUREAS AND THEIR METALLIC COMPLEXES. PART II. COMPLEX COMPOUNDS OF COPPER

By R. L. Dutta and Priyadaranjan Rây*

The preparation and properties of the complex compounds of copper with a number of guanylalkylureas, which include guanylmethyl-, -ethyl-, -*iso*propyl-, -*n*-butyl-, -*iso*butyl-, -*iso*amyl-, -*n*-hexyl- and -benzyl-ureas, have been described. All the *bis*-guanylurea copper complexes are rose red in colour. Determination of the equivalent conductivity of some of these reveal their bi-univalent character. A comparatively low value for the magnetic moment for the copper atom in these complexes indicates their planar structure with dsp^2 hybrid bonds.

By treating the aqueous solution of the complex copper *bis*-guanylmethylurea or copper *bis*-guanylethylurea chloride with dilute HCl, deep blue copper *mono*-guanylmethyl- and -ethyl-urea chlorides have been obtained. These in aqueous solution undergo transformation to the rose-red *bis*-complexes.

As these compounds resemble more or less closely the copper biguanide complexes, their structure may be represented by a configuration similar to that for the latter, as proposed by Rây and Saha (this *Journal*, 1937, **14**, 670).

Unsubstituted guanylurea has long been known to form complexes with copper(II), nickel(II) and palladium(II) as basic hydroxides of the composition, $M(C_2H_5N_4O)_2,2H_2O$, where M = Cu, Ni or Pd (Haag, *Annalen*, 1862, **122**, 31; Grossmann and Schuck, *Ber.*, 1906, **39**, 3356; 1910, **43**, 674). Some salts of these complex copper and palladium bases have been described rather lately by Rây and Bandopadhyay (this *Journal*, 1952, **29**, 865). They, however, failed to isolate any salt of the complex nickel base, as the latter in neutral or slightly acid solution changed readily into the simple nickel salts. The same authors (*loc. cit.*) have also described the complex bases of N^1-phenylguanylurea with these three metals, having the composition, CuX_2,NiX_2,H_2O and $PdX_2,3H_2O$; where $HX = C_6H_5.C_2H_5N_4O$, a molecule of phenylguanylurea. The complex copper base is red-violet and the complex nickel base is orange-yellow. But their salts (sulphate and chloride) are light blue and green respectively like the simple copper and nickel salts. While the complex nickel base was found to be diamagnetic, its salts showed paramagnetic moments, practically identical with that for simple nickel ion. The complex palladium base and its salts are light yellow, and are both diamagnetic. Rây and Bandopadhyay (*loc. cit.*) have also described the cobalt(III) complexes of guanylurea and N^1-phenylguanylurea having the composition, $Co(C_2H_5N_4O)_3$ and $Co(C_6H_5.C_2H_4N_4O)_3$, $1.5H_2O$, respectively. These form red diamagnetic crystals.

In Part I of this series (this *Journal*, 1959, **36**, 409) it has been reported that an alcohol (mono- or dihydric) and dicyandiamide in presence of copper acetate lead to the formation of the copper complex of the corresponding guanylalkylurea. This reaction was found to take place in the case of a variety of alcohols, namely, methyl, ethyl, *iso*propyl, *n*-butyl, *iso*butyl, *iso*amyl, *n*-hexyl and benzyl alcohol. With ethyleneglycol, a dihydric alcohol, ethylene-diguanylurea could be expected, but instead, the complex copper salt of guanylhydroxyethylurea was obtained.

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The preparation and properties of the following copper complexes of a number of guanylalkylureas are described here.

I. $[Cu(GauH)_2]X_2.nH_2O$, where GauH = a molecule of guanylalkylurea (guanylmethyl-, -ethyl-, -*iso*propyl-, -*n*-butyl-, -*iso*butyl-, -*iso*amyl-, -*n*-hexyl-, -benzyl-, or -hydroxyethylurea) and X = CH_3COO, $\frac{1}{2}SO_4$, Cl, Br, I, SCN, NO_3, $\frac{1}{2}CO_3$, ClO_4, NO_2, $\frac{1}{2}S_2O_6$, $\frac{1}{2}C_2O_4$, $\frac{1}{2}HPO_4$, etc. These compounds are all rose-red in colour. The solubility of the salts in water decreases with increase in the chain-length of the substituent, whereas that in alcohol increases. The equivalent conductivity values of the chloride salts of the copper guanylmethylurea and guanylethylurea in water are in fair agreement with that for bi-univalent electrolytes. They all show a magnetic moment value of 1.6 to 1.8 μ_B.

II. $[Cu(Gau)_2]$, where GauH = a molecule of guanylalkylurea.

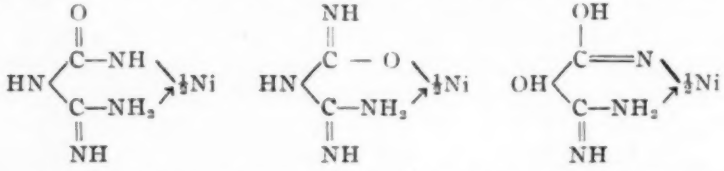
The rose-coloured complex copper *bis*-guanylalkylurea bases conform to the composition of anhydrobases. Their solutions in water or aqueous alcohol remain unchanged on boiling. In this respect, they are more stable than the corresponding base of the parent body, the simple guanylurea, which decomposes with separation of $Cu(OH)_2$ under the same condition.

III. $\begin{bmatrix} GauH \\ Cu \\ Cl_2 \end{bmatrix}$, where GauH = a molecule of guanylmethylurea or guanylethylurea.

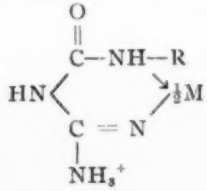
These copper *mono*-guanylalkylurea complexes are deep blue in colour and are formed at *p*H 4.0. In aqueous solution, they undergo transformation to the rose-red *bis*-complex:

$$2\begin{bmatrix} GauH \\ Cu \\ Cl_2 \end{bmatrix} \rightleftharpoons [Cu(GauH)_2]Cl_2 + CuCl_2$$

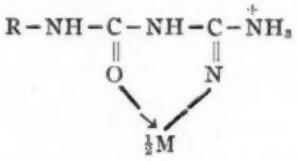
The following structures were assigned to the complex nickel guanylurea base by Tschugaeff (*Ber.*, 1907, **40**, 1975) and by Dumont (*Metallwirtschaft*, 1929, **7**, 281).



The constitution of guanylurea is related to those of biuret and biguanides. As the nickel and copper complexes of the guanylurea base are yellow and rose-red respectively, resembling the corresponding biguanide complexes, the structure of the former might be represented by a configuration similar to that of the latter, after Rây and Saha (this *Journal*, 1937, **14**, 670), as shown below:



where R = H or an alkyl group, and M = bivalent metal. An alternative structure :



might as well be suggested But in view of the fact that copper affords green-coloured complexes with acyloin oximes in which it links with both nitrogen and oxygen atoms, this configuration is rather improbable. Besides, oxygen is likely to be unavailable for co-ordination with the metal atom due to the possible formation of hydrogen bond.

Slotta and Tschesche's statement (*Ber*, 1928, **62**, 1390), that methylguanylurea or guanylmethylurea fails to give any coloured complex with copper, cannot be justified in the light of our present investigation. It appears that the products obtained by them are not actually the guanylmethyl- or methylguanyl-ureas as assumed on the basis of their estimation.

EXPERIMENTAL

General Method of Preparation of the Complex Copper Guanylalkylurea Compounds

Dicyandiamide (3 *M*), copper acetate (1 *M*) and the alcohol in excess were refluxed on the water-bath for 3 to 4 hrs. The red-violet solution was filtered and the filtrate on keeping in the cold deposited shining crystals of the complex copper *bis*-guanylalkylurea acetates. These were further purified by recrystallisation from water or rectified spirit, as the case may be. Substitution of copper chloride for copper acetate produces the copper guanylalkylurea chloride.

The complex copper *bis*-guanylalkylurea sulphate and other salts were obtained by the addition of an aqueous solution of alkali metal salt of the corresponding anion to that of the complex acetate. The complex copper salts of guanylmethylurea and of guanylethylurea, with the exception of the chloride, thiocyanate and acetate, are insoluble in water and in alcohol. As the solubility of the complex salts in alcohol increases with increase in the chain-length of the substituent, it has been possible to purify many of the complex copper salts of guanyl-*iso*propyl-, -*iso*butyl-, -*n*-butyl-, -*iso*amyl-, -*n*-hexyl- and -benzylurea by recrystallisation from warm alcohol.

The complex copper *bis*-guanylalkylurea bases were prepared by the addition of alkali to an aqueous or alcoholic solution of the complex copper acetate or chloride. These were recrystallised from hot water or alcohol.

The hydrated complex copper guanylalkylurea carbonates lose CO_2 and H_2O at 110° and are converted into the corresponding anhydrobases.

Copper mono-*guanylmethyl-* and mono-*guanylethyl-urea chlorides* were prepared by the addition of 3*N*-HCl to an aqueous solution of their corresponding complex copper *bis*-guanylalkylurea chloride till the solution turned from red-violet to deep blue (*p*H 3.8 to 4.0). The solution was then concentrated on the water-bath and allowed to stand, when deep blue crystals of copper *mono*-guanylmethyl- or -ethylurea chloride separated out. The crystals were filtered and washed with cold alcohol to remove the adhering copper chloride. In contact with water they suffer transformation to the complex copper *bis*-guanylmethyl or -ethylurea chloride with liberation of copper chloride.

TABLE I

Complex compounds of copper with guanylmethylurea.

			Found.	Calc.
1.	Copper *bis*-guanyl-methylurea $[Cu(x)_2]$	Cu	: 21.90%	21.63%
		N	: 37.80	38.12
2.	Acetate $[Cu(xH)_2]\cdot(CH_2COO)_2, 2.5H_2O$	Cu	: 14.00	13.84
		N	: 24.88	24.42
		*H_2O	: 10.25	9.81
3.	Sulphate $[Cu(xH)_2]SO_4, 3.5H_2O$	Cu	: 14.08	14.00
		N	: 25.13	24.72
		SO_4	: 21.23	21.19
		*H_2O	: 14.52	14.00
4.	Chloride $[Cu(xH)_2]Cl_2$	Cu	: 17.36	17.32
		N	: 30.17	30.55
		Cl	: 19.27	19.36
5.	Bromide $[Cu(xH)_2]Br_2$	Cu	: 14.36	13.96
		N	: 25.00	24.60
		Br	: 35.00	35.12
6.	Iodide $[Cu(xH)_2]I_2$	Cu	: 11.41	11.55
		N	: 20.60	20.38
		I	: 45.99	46.22
7.	Thiocyanate $[Cu(xH)_2](SCN)_2$	Cu	: 15.53	15.43
		SCN	: 27.94	28.13
8.	Nitrate $[Cu(xH)_2](NO_3)_2$	Cu	: 15.39	15.13
		N	: 33.75	33.37
9.	Carbonate $[Cu(xH)_2]CO_3, 3H_2O$	Cu	: 15.73%	15.73%
		N	: 27.10	27.75
		CO_2 & H_2O (by loss at 120°)	27.88	28.74
10.	Perchlorate $[Cu(xH)_2](ClO_4)_2$	Cu	: 13.23	12.84
		N	: 22.43	22.64
11.	Nitrite $[Cu(xH)_2](NO_2)_2$	Cu	: 16.58	16.38
12.	Dithionate $[Cu(xH)_2]S_2O_6$	Cu	: 14.18	13.94
		S_2O_6	: 35.40	35.12
13.	Oxalate $[Cu(xH)_2]C_2O_4, 3.5H_2O$	Cu	: 14.55	14.22
		N	: 24.80	25.08
		C_2O_4	: 19.47	19.78
		*H_2O	: 13.88	14.11
14.	Phosphate $[Cu(xH)_2]HPO_4, 5.5H_2O$	Cu	: 12.90	12.94
		N	: 22.78	22.83
		*H_2O	: 20.15	20.18
15.	Copper *mono*-guanyl-methylurea chloride $[Cu(xH)Cl_2]$	Cu	: 25.07	25.34
		N	: 22.55	22.35
		Cl	: 27.95	28.34

* H_2O by loss at 110°.

[xH stands for guanylmethylurea, $C_3H_8N_4O$].

TABLE II

Complex compounds of copper with guanylethylurea.

			Found.	Calc.
1.	Copper *bis*-guanylethylurea $[Cu(x)_2]$	Cu	: 19.95%	19.75%
		C	: 29.85	29.86
		H	: 5.62	5.59
		N	: 35.10	34 83
2.	Acetate $[Cu(xH)_2](CH_3COO)_2.4.5H_2O$	Cu	: 11.93	12.15
		N	: 21.65	21.48
		*H_2O	: 15.36	15.50
3.	Sulphate $[Cu(xH)_2]SO_4,3H_2O$	Cu	: 13 28	13.41
		N	: 23.20	23,65
		SO_4	: 19.96	20.27
		*H_2O	: 11.47	11.40
4.	Chloride $[Cu(xH)_2]Cl_2,1.5H_2O$	Cu	: 15.04	15.06
		N	: 26.86	26.57
		Cl	: 16.75	16.84
		*H_2O	: 6.70	6.41
5.	Bromide $[Cu(xH)_2]Br_2,2H_2O$	Cu	: 12.42	12 22
		N	: 21.95	21.55
		Br	: 31.30	30.79
		*H_2O	: 6.67	6.92
6	Iodide $[Cu(xH)_2]I_2$	Cu	: 11.14	10.99
		N	: 19.35	19.39
		I	: 44.20	43.98
7.	Thiocyanate $[Cu(xH)_2](SCN)_2$	Cu	: 14.95	14.44
		SCN	: 26.93	26.38
8.	Nitrate $[Cu(xH)_2](NO_3)_2.H_2O$	Cu	: 13.85%	13.86%
		N	: 30.00	30.00
9.	Carbonate $[Cu(xH)_2]CO_3,5H_2O$	Cu	: 13.43	13 41
		N	: 23.70	23.65
		*$\{CO_2+H_2O$	: 33.21	32.10
10.	Perchlorate $[Cu(xH)_2](ClO_4)_2$	Cu	: 12 10	12.15
		N	: 21.90	21.43
11.	Nitrite $[Cu(xH)_2](NO_2)_2$	Cu	: 15.35	15.28
12.	Dithionate $[Cu(xH)_2]S_2O_6,H_2O$	Cu	: 12.96	12.66
		*H_2O	: 3.45	3.51
13.	Oxalate $[Cu(xH)_2]$-$C_2O_4,3.5H_2O$	Cu	: 13.43	13.38
		N	: 23.00	23.60
		$H_2C_2O_4$	: 19.47	18 96
		*H_2O	: 13.30	13.27
14.	Chromate $[Cu(xH)_2]CrO_4,2H_2O$	Cu	: 13.60	13.35
		Cr	: 11.09	10.93
15.	Copper *mono*-guanylethylurea chloride $[Cu(xH)Cl_2]$	Cu	: 23.48	24.00
		N	: 21.73	21.17
		Cl	: 26.93	26.84

* By loss at 110°.
[xH stands for guanylethylurea, $C_4H_{10}N_4O$].

TABLE III

*Complex compounds of copper with guanyliso*propylurea.

			Found.	Calc.
1.	Copper *bis*-guanyl*iso*-propylurea $[Cu(x)_2]$	Cu	: 18.03%	18.17%
		N	: 31.73	32.04
2.	Acetate $[Cu(xH)_2](CH_3COO)_2,3.5H_2O$	Cu	: 12.22	11.92
		N	: 20.56	21.03
		*H_2O	: 11.32	11.83
3.	Sulphate $[Cu(xH)_2]SO_4,H_2O$	Cu	: 13.43	13.63
		N	: 24.28	24.06
		SO_4	: 20.24	20.62
4.	Chloride $[Cu(xH)_2]Cl_2,2H_2O$	Cu	: 13.79	13.84
		*H_2O	: 8.00	7.84
5.	Bromide $[Cu(xH)_2]Br_2,1.5H_2O$	Cu	: 11.88%	11 79%
		Br	: 29.45	29.69
6.	Iodide $[Cu(xH)_2]I_2,2H_2O$	Cu	: 9.81	9.89
		I	: 39.90	39.59
		*H_2O	: 5.49	5.61
7.	Nitrate $[Cu(xH)_2](NO_3)_2$	Cu	: 13.28	13.35
8.	Carbonate $[Cu(xH)_2]CO_3,4H_2O$	Cu	: 13.30	13.13
		N	: 23.45	23.16
		CO_2+H_2O (by loss at 120°)	: 28.30	27.71

* By loss at 110°.
[xH stands for guanyl*iso*propylurea, $C_5H_{12}N_4O$].

TABLE IV

Complex compounds of copper with guanyl-n-butylurea.

		Found.	Calc.			Found.	Calc.
1. Copper *bis*-guanyl-*n*-butylurea $[Cu(x)_2]$	Cu	: 16.70%	16.82%	6. Thiocyanate $[Cu(xH)_2](SCN)_2.H_2O$	Cu	: 12.10%	12.37%
	N	: 29.06	29.67		SCN	: 23.03	22.60
2. Acetate $[Cu(xH)_2](CH_3COO)_2.1.5H_2O$	Cu	: 12.12	12.11	7. Nitrate $[Cu(xH)_2](NO_3)_2.H_2O$	Cu	: 12.21	12 18
	N	: 21.23	21.35		*H_2O	: 3.45	3.45
3. Sulphate $[Cu(xH)_2]SO_4,1.5H_2O$	Cu	: 12.63	12.63	8. Perchlorate $[Cu(xH)_2](ClO_4)_2.0.5H_2O$	Cu	: 10.85	10.82
	N	: 21.90	22.28		N	: 18.73	19 06
	SO_4	: 18.51	19.11				
	*H_2O	: 5.32	5.35	9. Nitrite $[Cu(xH)_2](NO_2)_2$	Cu	: 13 23	13.47
4. Chloride $[Cu(xH)_2]Cl_2,2H_2O$	Cu	: 13.03	13.05				
	Cl	: 14.61	14.58	10. Dithionate $[Cu(xH)_2S_2O_6.H_2O$	Cu	: 11.27	11.38
	*H_2O	: 7.44	7.40		N	: 20.19	20.03
					*H_2O	: 2 91	3.22
5. Bromide $[Cu(xH)_2]Br_2,2H_2O$	Cu	: 11.00	11.05				
	Br	: 28.00	27.80	11. Phosphate $[Cu(xH)_2]HPO_4, 2H_2O$	Cu	: 12.82	12.41
	N	: 19.40	19.46				
	*H_2O	: 5.41	6.25				

* By loss at 110°.
[xH stands for guanyl-*n*-butylurea, $C_6H_{14}N_4O$].

TABLE V

Complex compounds of copper with guanylisobutylurea.

		Found.	Calc.			Found.	Calc.
1. Copper *bis*-guanyl*iso*-butylurea $[Cu(x)]_2$	Cu	: 16,89	16.82	5. Bromide $[Cu(xH)_2]Br_2$, $1.5H_2O$	Cu	: 11.12	11.21
	N	: 29.40	29.67		Br	: 28.70	28.24
					*H_2O	: 4.57	4.76
2. Acetate $[Cu(xH)_2](CH_3COO)_2,2H_2O$	Cu	: 12.00	11.90	6. Thiocyanate $[Cu(xH)_2](SCN)_2, H_2O$	Cu	: 12.12	12.37
	N	: 20.85	21.00		SCN	: 22.64	22.60
	*H_2O	: 6.40	6.75		*H_2O	: 3 41	3 56
3. Sulphate $[Cu(xH)_2]SO_4$	Cu	: 13.45	13.35	7. Nitrate $[Cu(xH)_2](NO_3)_2,2H_2O$	Cu	: 11.63	11.77
	N	: 23.79	23.55		*H_2O	: 6.20	6.67
	SO_4	: 19.72	20.19				
4. Chloride $[Cu(xH)_2]Cl_2,2H_2O$	Cu	: 12.78	13.06	8. Perchlorate $[Cu(xH)_2](ClO_4)_2$	Cu	: 10.92	10.96
	Cl	: 14.74	14.59		N	: 19.00	19.36
	*H_2O	: 6.94	7.40				

* By loss at 110°.
[xH stands for guanyl*iso*butylurea, $C_6H_{14}N_4O$].

TABLE VI

Complex compounds of copper with guanylisoamylurea.

		Found.	Calc.
1.	Copper *bis* guanyl*iso*amylurea $[Cu(x)_2]$	Cu : 15.25% N : 27.40	15.66% 27.63
2	Acetate $[Cu(xH)_2](CH_3COO)_2, H_2O$	Cu : 11.81 N : 20.60 *H_2O : 3.49	11.68 20.60 3.29
3.	Sulphate $[Cu(xH)_2]SO_4, 0.5H_2O$	Cu : 12.52 SO_4 : 19.00 *H_2O : 1.68	12.39 18.74 1.74
4.	Chloride $[Cu(xH)_2]Cl_2,2H_2O$	Cu : 12 49 Cl : 14.22 *H_2O : 3.40	12.79 14.30 3.62
5.	Bromide $[Cu(xH)_2]Br_2$	Cu : 10.90 Br : 28.10	11.19 28.20
6.	Thiocyanate $[Cu(xH)_2](SCN)_2, 2H_2O$	Cu : 11.43 SCN : 20 79	11.36 20.75
7.	Nitrate $[Cu(xH)_2](NO_3)_2, 2H_2O$	Cu : 11.34 *H_2O : 6.20	11.19 6 35
8.	Perchlorate $[Cu(XH)_2](ClO_4)_2$	Cu : 10.82	10.47

*By loss at 110°

[xH stands for guanyl*iso*amylurea, $C_7H_{16}N_4O$].

TABLE VII

Complex compounds of copper with guanyl-n-hexylurea.

		Found.	Calc.
1.	Copper *bis*-guanyl-*n*-hexyl-urea base $[Cu(x)_2]$	Cu : 14.88% N : 25.40	14.64% 25.83
2.	Acetate $[Cu(xH)_2](CH_3COO)_2, 1.5H_2O$	Cu : 11.00 N : 19.53	10.90 19.22
3.	Sulphate $[Cu(xH)_2]SO_4, 0.5H_2O$	Cu : 11 95 N : 21.03 SO_4 : 17.88	11.70 20.64 17 69
4.	Chloride $[Cu(xH)_2]Cl_2, 0 5H_2O$	Cu : 12.01 Cl : 13.52	12.27 13.71
5.	Bromide $[Cu(xH)_2]Br_2,H_2O$	Cu : 10.11 Br : 25 90 *H_2O : 3.03	10.31 25.99 2.92
6.	Nitrate $[Cu(xH)_2](NO_3)_2, 2H_2O$	Cu : 10.56 *H_2O : 6.41	10.62 6 00
7.	Perchlorate $[Cu(xH)_2](ClO_4)_2$	Cu : 10.04 N : 17.84	9.97 17 59
8	Dithionate $[Cu(xH)_2]S_2O_6, 0.5H_2O$	Cu : 10 39	10.46

*By loss at 110°.

[xH stands for guanyl-*n*-hexylurea, $C_8H_{18}N_4O$].

TABLE VIII

Complex compounds of copper with guanylbenzylurea.

		Found.	Calc.
1.	Copper *bis*-guanylbenzylurea $[Cu(x)_2]$	Cu : 14.31	14 23
2.	Acetate $[Cu(xH)_2](CH_3COO)_2, H_2O$	Cu : 10.88 N : 18.91	10.88 19.19
3.	Sulphate $[Cu(xH)_2]SO_4, 3H_2O$	Cu : 10.79 N : 18.91 SO_4 : 15.86 *H_2O : 8.52	10.62 18.74 16.06 9.03
4.	Chloride $[Cu(xH)_2]Cl_2,3H_2O$	Cu : 11.28 Cl : 11.92	11.09 12.40
5.	Bromide $[Cu(xH)_2]Br_2$	Cu : 9.49 Br : 24.25	9.59 24.16
6.	Thiocyanate $[Cu(xH)_2](SCN)_2$	Cu : 10.64 SCN : 18 79	10.43 19.06

*By loss at 110°.

[xH stands for guanylbenzylurea, $C_9H_{12}N_4O$].

Complex Compounds of Copper with Guanylhydroxyethylurea

Copper bis-*guanylhydroxyethylurea Sulphate.*—Dicyandiamide (2 g.) was taken in ethyleneglycol (60 c.c.) and dissolved by warming (60°) on the water-bath. Copper acetate dihydrate (2 g.) was added in small portions at a time within 10 minutes with regular stirring, and the mixture maintained at that temperature for about 15 mins. Further heating brings about decomposition of the complex. The resulting red-violet thick solution was filtered, the filtrate cooled and treated with a strong solution of ammonium sulphate. A rose-coloured precipitate was obtained. This was filtered and dissolved in H_2SO_4 (dil.) in the cold and the product reprecipitated by the addition of ammonium hydroxide and ammonium sulphate. This was filtered, washed first with water, then with alcohol, and finally dried in air. The substance suffers some decomposition on boiling with water. { Found : Cu, 12.96 ; N, 22.66 ; SO_4, 19.83 ; H_2O (by loss at 110°), 7.72. $[Cu(C_4H_{11}N_4O_2)_2]SO_4, 2H_2O$ requires Cu, 12.99 ; N, 22.88 ; SO_4, 19.61 ; H_2O, 7.35% }.

Equivalent Conductivity

Measurements of conductivity at different dilutions were carried out at 35°. The equivalent conductivity at infinite dilution was then calculated with the help of Walden's formula $\Lambda_\infty = \Lambda_v (1 + 0.692 \times n_1 \times n_2 \times v^{-\frac{1}{2}})$ where n_1 and n_2 are the valencies of the ions.

TABLE IX

A. Copper *bis*-guanylmethylurea chloride.

Dilution (in litres) ...	32	64	128	256	512	1024
Λ_v ...	96.5	104.2	106.8	109.1	118.1	119.9
Λ_∞ ...	120.0	119.6	119.8	118.5	125.3	125.3
Λ_∞ (mean) ...	121.4					
Mol. conductivity ...	242.8					

B. Copper *bis*-guanylethylurea chloride.

Dilution ...	32	64	128	256	512	1024
(in litres).	99.38	104.6	106.8	118.6	127.2	141.8
Λ_v ...						
Λ_∞ ...	123.7	120.1	120.0	128.8	135.0	147.8
Λ_∞ (mean) ...	129.2					
Mol. conductivity ...	258.4					

Magnetic Susceptibility

The magnetic susceptibility of some of the copper guanylalkylurea complexes was determined by following Gouy's method. The results of measurements are recorded in Table X.

TABLE X

Substance.	$\chi_g \times 10^6$.	$\chi_M \times 10^6$.	Dia. corr $\times 10^6$.	χ_M (corr.) $\times 10^6$.	μ_B.
Copper *bis*-guanylmethylurea sulphate $[Cu(C_3H_8N_4O)_2]SO_4,3.5H_2O$	2.101	954.0	155.6	1109.0	1.65
Copper *bis*-guanylethylurea sulphate $[Cu(C_4H_{10}N_4O)_2]SO_4,3H_2O$	2.396	1131.5	173.2	1304.7	1.79
Copper *bis*-guanyl*iso*propylurea acetate $[Cu(C_5H_{12}N_4O)_2](CH_3COO)_2.3.5H_2O$	1.582	842.4	220.2	1062.0	1.62
Copper *bis*-guanyl-*n*-butylurea chloride $[Cu(C_6H_{14}N_4O)_2]Cl_2,2H_2O$	2.605	1035.0	220.4	1255.0	1.75
Copper *bis*-guanyl*iso*amylurea chloride $[Cu(C_7H_{16}N_4O)_2]Cl_2.H_2O$	2.309	1151.0	232.0	1383.0	1.84
Copper *bis*-guanyl-*n*-hexylurea chloride $[Cu(C_8H_{18}N_4O)_2]Cl_2,0.5H_2O$	1.775	918.7	249.6	1168.0	1.69

A comparatively low value for the magnetic moment of the copper atom is indicative of the compounds possessing a planar structure with dsp^2 hybrid bonds, characteristic of the inner-level or penetration complexes (Rây and Sen, this *Journal*, 1948, **25**, 475).

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GUANYLALKYLUREAS AND THEIR METALLIC COMPLEXES. PART III. COMPLEX COMPOUNDS OF NICKEL

By R. L. Dutta and Priyadaranjan Rây*

The preparation and properties of complex compounds of nickel (II) with guanylalkylureas have been described. These are all yellow to orange-yellow in colour. Their diamagnetic nature indicates a planar structure with dsp^2 hybrid bonds.

In the preceding part of this series (this *issue*, p. 567) the preparation and properties of the complex compounds of copper with a number of guanylalkylureas have been described. The present paper deals with the corresponding nickel complexes. These are represented by :

I. $[Ni(GauH)_2]\ X_2.nH_2O$, where GauH = a molecule of guanylalkylurea (guanylmethyl-, -ethyl-, -*iso*propyl-, -*n*-butyl-, -*iso*butyl-, -*iso*amyl- and -*n*-hexyl-urea) and X = Cl, $\frac{1}{2}SO_4$, Br, I, SCN, ClO_4, NO_3, $\frac{1}{2}S_2O_6$, etc.

II. $[Ni(Gau)_2]$, where GauH = a molecule of guanylalkylurea (guanylmethyl-, -ethyl-, -*iso*propyl-, -*n*-butyl-, -*iso*butyl- or -*iso*amyl-urea).

III. $[Ni(GauH)_2]\ (OH)_2$, where GauH = a molecule of guanyl-*n* hexylurea.

All these complex nickel compounds are orange-yellow in colour, and are not decomposed on boiling their aqueous or alcoholic solutions. The complex nickel base of unsubstituted guanylurea, on the other hand, decomposes with separation of nickel hydroxide under the same condition. Their solubility in water decreases with increase in the chain-length of the substituent in the guanylurea molecule, whereas that in alcohol increases. The equivalent conductivity values of the chloride salts of the nickel guanylmethylurea and nickel guanylethylurea in water are in fair agreement with those for a bi-univalent electrolyte. They are all diamagnetic, which indicates a planar structure, characteristic of penetration complexes of nickel with dsp^2 bonds.

Experimental

Nickel bis-*Guanylmethylurea*.—An aqueous solution of nickel sulphate heptahydrate (1 *M*) was added to that of the guanylmethylurea sulphate (1.5 *M*) and the mixture was made strongly alkaline with NaOH solution. The complex nickel base separated as a bright yellow crystalline precipitate. The mixture was digested on the water-bath for some time. The precipitate was then filtered, washed withwater and dried over $CaCl_2$ and KOH.

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The substance is insoluble in cold water but soluble in hot water, and also in alcohol. It liberates ammonia from ammonium salts, and reacts alkaline in solution.

Nickel bis-*guanylmethylurea chloride* was obtained by digesting the base on the water-bath with a strong solution of ammonium chloride till the evolution of ammonia had ceased. The mixture was cooled, when the crystals of the complex chloride separated in quantity. These were filtered and recrystallised from hot water.

The same compound was, however, more conveniently prepared by triturating the complex base with HCl (2*N*) to a neutral reaction and then purified by recrystallisation from water. The substance forms bright orange-yellow crystals.

The complex nickel bases of the other guanylalkylureas were obtained from nickel sulphate and the corresponding guanylalkylurea sulphate by the action of an excess of NaOH. The complex chlorides were prepared by triturating the complex bases with dilute HCl. The other salts of the complex bases were obtained as light orange-yellow crystalline precipitates by double decomposition from the complex chloride and the appropriate alkali metal salt in aqueous-alcoholic solution. Many of these compounds were further purified by crystallisation from alcohol. The results of analysis showing their composition are recorded in the following tables.

TABLE I

Complex compounds of nickel with guanylmethylurea.

		Found.	Calc.
1.	Nickel *bis*-guanylmethylurea	Ni : 20.20%	20.33%
	$[Ni(x)_2]$	N : 38.90	38.75
2.	Chloride	Ni : 16.13	16.22
	$[Ni(xH)_2]Cl_2$	Cl : 19.88	19.62
		N : 31.05	30.96
3.	Sulphate	Ni : 13.04	13.31
	$[Ni(xH)_2]SO_4,3H_2O$	SO_4 : 21.87	21.78
		N : 25.98	25.41
		H_2O : 12.37 (by loss at 110°)	12.25
4.	Nitrate	Ni : 14.49	14.15
	$[Ni(xH_2](NO_3)_2$	N : 33.32	33.75
5.	Dithionate	Ni : 11.67	11.84
	$[Ni(xH)_2]S_2O_6,2.5H_2O$	S_2O_6 : 31.80	32.39

[xH stands for guanylmethylurea, $C_3H_8N_4O$].

TABLE II

Complex compounds of nickel with guanylethylurea.

		Found.	Calc.
1.	Nickel *bis*-guanylethylurea $[Ni(x)_2]$	Ni : 18.29% N : 35.42	18.53% 35.36
2.	Chloride $[Ni(xH)_2]Cl_2,2H_2O$	Ni : 13.80 Cl : 16.88 N : 26 36 *H_2O : 8.37	13.78 16.67 26.30 8 45
3	Sulphate $[Ni(xH)_2]SO_4,7H_2O$	Ni : 10.60 SO_4 : 17.55 *H_2O : 22 90 $\chi_g = -0.041 \times 10^{-6}$	10.85 17.75 23 30
4.	Bromide $[Ni(xH)_2]Br_2,H_2O$	Ni : 12.08 Br : 32.00	11.81 32.21
5.	Iodide $[Ni(xH)_2]I_2$	Ni : 10.06 I : 44.00	10.23 44 35
6.	Perchlorate $[Ni(xH)_2](ClO_4)_2$	Ni : 11.08	11.33

*By loss at 110°
[xH stands for guanylethylurea $C_4H_{10}N_4O$].

TABLE III

Complex compounds of nickel with guanyl-isopropylurea.

		Found.	Calc.
1.	Nickel *bis*-guanyl*iso*propylurea $[Ni(x)_2]$	Ni : 17.27% N : 32.80	17.02% 32 49
2.	Chloride $[Ni(xH)_2]Cl_2,2.5H_2O$	Ni : 12.49 Cl : 15.71 $\chi_g = -0\ 052 \times 10^{-6}$	12.67 15 34
3.	Sulphate $[Ni(xH)_2]SO_4,H_2O$	Ni : 12.68 SO_4 : 21.08	12.70 20.82

[xH stands for guanyl *iso*propylurea, $C_5H_{12}N_4O$].

TABLE IV

Complex compounds of nickel with guanyl-n-butylurea.

		Found.	Calc.
1.	Nickel *bis*-guanyl-*n*-butylurea $[Ni(x)_2]$	Ni : 15.56% N : 29 88	15.66% 29.88
2.	Chloride $[Ni(xH_2]Cl_2,0.5H_2O$	Ni : 12.91 Cl : 15.03 $\chi_g = -0\ 08 \times 10^{-6}$	12.66 15.31
3.	Sulphate $[Ni(xH)_2]SO_4,4H_2O$	Ni : 11.04 SO_4 : 17.84 H_2O : 13.56 (by loss at 110°)	10.81 17.68 13.26
4.	Nitrate $[Ni(xH)_2](NO_3)_2$	Ni : 11.83	11.77

[xH stands for guanyl-*n*-butylurea, $C_6H_{14}O_4$].

TABLE V

Complex compounds of nickel with guanylisobutylurea.

		Found.	Calc.
1.	Nickel *bis*-guanyl*iso*butylurea $[Ni(x)_2]$	Ni : 15.36% N : 29.75	15.66% 29 88
2.	Chloride $[Ni(xH)_2]Cl_2,2H_2O$	Ni : 12.10 Cl : 14.74	12.19 14.74
3.	Sulphate $[Ni(xH)_2]SO_4,0.5H_2O$	Ni : 12.25 SO_4 : 19.83 H_2O : 2.12 (by loss at 110°)	12 24 20.02 1 86

[xH stands for guanyl*iso*butylurea, $C_6H_{14}N_4O$].

TABLE VI

Complex compounds of nickel with guanyliscamylurea.

		Found.	Calc.
1.	Nickel *bis*-guanyl*iso*amylurea $[Ni(x)_2]1.5H_2O$	Ni : 13.54% N : 26 70	13.73% 26.25
2.	Chloride $[Ni(xH)_2]Cl_2,2H_2O$	Ni : 11 25 Cl : 14 04 $\chi_g = -0.06 \times 10^{-6}$	11.51 13.92
3.	Sulphate $[Ni(xH)_2SO_4,0.5H_2O$	Ni : 11.48 SO_4 : 19.05	11 56 18.91
4.	Bromide $[Ni(xH)_2]Br_2$	Ni : 10.48 Br : 28.50	10.43 28.44
5.	Iodide $[Ni(xH)_2]I_2$	Ni : 8.95	8.94
6.	Nitrate $[Ni(xH)_2](NO_3)_2,1.5H_2O$	Ni : 10.39 H_2O : 4.82 (by loss at 110°)	10.60 4.87

[xH stands for guanyl*iso*amylurea, $C_7H_{16}N_4O$].

TABLE VII

Complex compounds of nickel with guanyl-n-hexylurea.

		Found.	Calc.
1.	Nickel *bis*-guanyl-*n*-hexylurea hydroxide $[Ni(xH)_2](OH)_2$	Ni : 12.56% N : 24.35	12.63% 24.10
2.	Chloride $[Ni(xH)_2]Cl_2$	Ni : 11.82 Cl : 13.84	11.70 14.15
3.	Sulphate $[Ni(xH)_2]SO_4$	Ni : 10.97 SO_4 : 17.80 N : 20.63	11.14 18.22 21.26

[xH stands for guanyl-*n*-hexylurea, $C_8H_{18}N_4O$].

Equivalent Conductivity

Measurements of conductivity at different dilutions were carried out at 35°. The equivalent conductivity at infinite dilution was then calculated with the help of Walden's formula :

$\Lambda_\infty = \Lambda_v(1 + 0.692 \times n_1 \times n_2 \times v^{-\frac{1}{2}})$; where n_1 and n_2 are the valencies of the ions.

TABLE VIII

A. Nickel *bis*-guanylmethylurea chloride $[Ni(C_3H_8N_4O)_2]Cl_2$.

Dilution v (in litres)	...	32	64	128	256	512	1024
Λ_v	...	97.7	105.3	107.3	113 6	126.3	127.2
Λ_∞	...	121 5	123.5	120.4	123.4	134.0	132 7
Λ_∞ (mean)	...	125.5					

Mol. conductivity ... 251

B. Nickel *bis*-guanylethylurea chloride $[Ni(C_4H_{10}N_4O)_2]\ Cl_2{,}2H_2O$.

Dilution v (in litres)	...	32	64	128	256	512	1024
Λ_v	...	90 8	96.6	93.9	118.2	127.2	138.1
Λ_∞	...	113.0	111	112	128.4	135	144
Λ_∞ (mean)	...	123.9					

Mol. conductivity ... 247.8

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HYDROXY- AND ALKOXY-ALKYLBIGUANIDE METAL COMPLEXES. PART III. COBALT AND CHROMIUM COMPLEXES

By Nihar Ranjan Sengupta and Priyadaranjan Rây*

Out of all the hydroxy- and alkoxy-alkylbiguanides, it has been possible to isolate the cobalt(III) and chromium(III) complexes of ethanolbiguanide only. Preparation and properties of these complexes have been described.

The preparations and properties of copper, nickel and palladium complexes with hydroxy- and alkoxy-alkylbiguanides have been described previously (Sengupta and Rây, this *Journal*, 1959, **36**, 373 489). The present work gives an account of the cobalt(III) and chromium(III) complexes of ethanolbiguanide only, as attempts to isolate similar complexes with other biguanides of this series were unsuccessful. Owing to their extremely hygroscopic nature, even the complex cobaltic *tris*-ethanolbiguanide base and chloride could not be obtained in a pure state. The other hydroxy- and alkoxy-alkylbiguanides form with cobaltous salts in alkaline solution yellow precipitates of complex cobaltous biguanides, which oxidise instantaneously to extremely soluble cobaltic compounds. These could not be isolated in the solid crystalline state.

With chromium(III), ethanolbiguanide forms a rose-coloured hydroxy-aquo-*bis*-ethanolbiguanide complex. The complex chromium base as well as its sulphate, chloride, bromide, iodide, nitrate, thiosulphate, etc. has been prepared and their properties have been studied. They all lose their complex-bound water even at 90°, giving rise to products with a diol-binuclear complex cation.

$$2\left[\mathrm{Cr(s-BigH)_2.}\begin{matrix}\mathrm{OH}\\ \mathrm{H_2O}\end{matrix}\right]\mathrm{X_2}\xrightarrow[-2\mathrm{H_2O}]{\text{At }90^\circ}\left[\mathrm{(s-BigH)_2Cr}\begin{matrix}\swarrow\mathrm{HO}\searrow\\ \searrow\mathrm{OH}\nearrow\end{matrix}\mathrm{Cr(s-BigH)_2}\right]\mathrm{X_4}$$

where s−BigH = one molecule of ethanolbiguanide, X = OH or any univalent anion, or an equivalent of a polyvalent anion.

The conductivity measurement of the hydroxo-aquo-chromium *bis*-ethanolbiguanide chloride in solution furnishes values which correspond to those of a bi-univalent salt in agreement with its constitution.

Experimental

Cobaltic tris-*Ethanolbiguanide Sulphate.*—Ethanolbiguanide sulphate (5.50 g.,) dissolved in minimum quantity of hot water, was treated with a solution of KOH (1.70 g. in 150 c.c. of absolute alcohol). The precipitated potassium sulphate was filtered off. The filtrate was treated with a solution of hexammine cobaltic chloride (2.49 g.) and digested on the water-bath till the evolution of ammonia had ceased. The colour of the solution changed from yellow to dark red. It was filtered and the filtrate evaporated to dryness on the water-bath. The residual

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mass was cooled in ice and cautiously neutralised with 6*N*-H_2SO_4. The mixture was then treated with absolute alcohol and digested on the water-bath for a few minutes. An oil separated from the solution, when the supernatant liquid was decanted off. The oily mass was then washed with alcohol by decantation a number of times (usually five or six). On cooling in an ice-bath and agitating with a fresh quantity of absolute alcohol, the oil solidified. This was dissolved in the minimum quantity of hot water and treated with absolute alcohol. The dark red crystalline precipitate, thus obtained, was filtered, washed with alcohol and immediately removed to a desiccator, where it was dried over $CaCl_2$. {Found : Co, 8.84 ; N, 32.43 ; SO_4, 21.18 ; H_2O (by loss at 110°), 5.34. $[Co(OH.C_2H_4.C_2N_5H_6)_3]_2(SO_4)_3,4H_2O$ requires Co, 8.74 ; N, 31.16 ; SO_4, 21.37 ; H_2O, 5.34% }.

The dark red complex cobaltic *tris*-ethanolbiguanide sulphate is extremely hygroscopic and soluble in water, but insoluble in alcohol, acetone, etc.

Hydroxo-aquo-chromium bis-*Ethanolbiguanide Complexes*

1. *Hydroxo-aquo-chromium* bis-*Ethanolbiguanide Sulphate.*—A solution of chrome alum (10 g.) in water (20 c.c.) was added dropwise at the room temperature with constant stirring to that of ethanolbiguanide (7 g. ethanolbiguanide sulphate and 2 g KOH in 50 c.c. of water). The mixture was then heated for a while on the water-bath and filtered. The deep red filtrate was cooled in ice and carefully neutralised with 18*N*-H_2SO_4 (1 : 1 by vol.), avoiding any rise in temperature during neutralisation. A rose-coloured complex sulphate separated from the solution on cooling. This was filtered, washed first with cold water, then with absolute alcohol and finally dried in air to a constant weight. { Found : Cr (iodometrically), 10.47 ; N, 28.11 ; SO_4, 19.39 ; H_2O (by loss at 110°), 9.18. $[Cr(OH.C_2H_4.C_2N_5H_6)_2(OH)H_2O]SO_4.1.5H_2O$ requires Cr, 10.40 ; N, 28.00 ; SO_4, 19.20 ; H_2O (including the complex bound water), 9.00% }.

Magnetic Susceptibility : χ_g at 32° = 13.89 × 10^{-6} ; χ_M = 6945 × 10^{-6} ; χ_A = 7150 × 10^{-6} ; μ_B = 4.19.

{Found for the substance dried at 110° : Cr, 11.46 ; SO_4, 21.07. $[Cr_2(OH.C_2H_4.C_2N_5H_6)_4(OH)_2](SO_4)_3$ requires Cr, 11.43 ; SO_4, 21.09 %}.

Properties.—The complex sulphate is sparingly soluble in water, but readily soluble in alkalies and insoluble in alcohol. It is easily decomposed by sodium peroxide. The aqueous suspension reacts weakly alkaline to litmus, but fails to liberate ammonia from ammonium salts.

2. The *complex base* was prepared by triturating in a mortar the complex sulphate (2.5 g.) and baryta (1.58 g.) in CO_2-free water (30-40 c.c.). The filtrate from barium sulphate was concentrated in vacuum over KOH and $CaCl_2$, and the rose-coloured complex base was precipitated by absolute alcohol. The product was filtered, washed first with ice-cold aqueous alcohol (1 : 4 by vol.), then with absolute alcohol and finally dried over KOH and $CaCl_2$. { Found : Cr, 11.90 ; N, 32.46 ; H_2O (by loss at 110°), 10.19. $[Cr(OH.C_2H_4.C_2N_5H_6)_2(OH)H_2O](OH)_2.1.5H_2O$ requires Cr, 11.87 ; N, 32.65 ; H_2O (including the complex bound water), 10.27% }.

3. *Complex Chloride.*—The complex sulphate (5.04 g.) and barium chloride ($BaCl_2.2H_2O$, 2.45 g.) were triturated in 50 c.c. of water in the cold. The filtrate from barium sulphate was allowed to concentrate in vacuum over H_2SO_4, when the rose-red complex chloride crystallised out. The crystals were filtered, washed first with ice-cold aqueous alcohol (1 : 4 by vol.), then with absolute alcohol. These were dried in air. { Found : Cr, 10.48 ; N, 27.96 ; Cl, 14.53 ; H_2O (by loss at 110°), 12.82. $[Cr(OH.C_2H_4.C_2N_5H_6)_2(OH)H_2O]Cl_2$, $2.5H_2O$ requires Cr, 10.54 ; N, 28.39 ; Cl, 14.40 ; H_2O (including the complex bound water), 12.75% }.

TABLE I

Conductivity measurement.

$t = 35°$.

Dilution (in litres) ...	*N*/256	*N*/512	*N*/1024	*N*/2048
Λ_v ...	129.5	140.9	150.9	154.8
Λ_∞ ...	135.1	145.2	154.0	156.8

Λ_∞ mean 147.8

The equivalent mobility of the complex ion $[Cr(OH.C_2H_4.C_2N_5H_6)_2(OH)H_2O]$ is equal to (147.8-85.0)=62.8, 85.0 being the mobility of Cl^- ion at 35°. The conductivity measurement indicates that in dilute solution the complex undergoes partial hydrolysis.

The other complex chromium salts, noted below, were prepared by adding the solution of the corresponding alkali salt to that of the complex chloride. These were washed and dried as usual.

TABLE II

Compounds.	Found.	Calc.
1. Bromide $[Cr\,X_2(OH)H_2O]\,Br_2,H_2O$	Cr : 9.33%	9.37%
	N : 25.64	25.20
	Br : 29.02	28.82
	H_2O : 6.57	6.49
2. Iodide $[Cr\,X_2(OH)H_2O]\,I_2,\,0.5H_2O$	Cr : 8.10	8.12
	N : 22.12	21.88
	I : 40.46	39.77
	H_2O : 4.21	4.22
3. Nitrate $[Cr\,X_2(OH)\,H_2O]\,(NO_3)_2$	Cr : 10.53	10.48
	N : 33.93	33.87
	H_2O : 3.52	3.63
4. Thiosulphate $[Cr\,X_2(OH)H_2O]\,S_2O_3,H_2O$	Cr : 10.12	10.26
	N : 28.16	27.62
	S_2O_3 : 22.50	22.09
	H_2O : 7.24	7.04
5. Dithionate $[Cr\,X_2(OH)H_2O]\,S_2O_6,3H_2O$	Cr : 8.91	8.80
	N : 24.26	23.69
	S_2O_6 : 26.65	27.05
	H_2O : 11.96	12.18
6. Chromate $[Cr\,X_2\,(OH)H_2O]\,CrO_4,\,1.5H_2O$	Cr : 20.40 (total)	20.00
	CrO_4 : 22.56	22.31
	H_2O : 8.64	8.67

$[X = OH.C_2H_4\,C_2N_5H_6]$

The loss of water indicates the loss of complex-bound water as well.

Properties.—Excepting the readily soluble complex chloride, all the other complex chromium salts are sparingly soluble in water. All the salts are stable in acids, but are easily decomposed by sodium peroxide. They all lose their complex-bound water molecule at 110° and thereby form diol-di-chromium *tetrakis*-ethanolbiguanide salts. With the exception of the complex chromate, which is yellow, all other salts are rose-coloured.

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β-PHENYLETHANOLAMINES. PART I. NEW SYNTHESIS OF AEGELINE AND PAPAVERINE

By N. Adityachaudhury and Mrs. A. Chatterjee

A simple method has been developed for the preparation of β-phenylethanolamines which has been extended in the syntheses of aegeline, *dl-trans-N*-(β-hydroxy-β-*p*-methoxyphenyl)-ethylcinnamamide, other acylamido-alcohols and papaverine.

β-Hydroxy-β-phenylethylamines are extensively used in clinical practice as pressor drugs for their sympathomimetic actions and antispasmodic properties. Several methods are available in the literature for their synthesis (Berger and Jowett, *J. Chem. Soc.*, 1905, **87**, 970 ; Rosenmund, *Ber.*, 1913, **46**, 1047 ; Kindler and Peschke, *Arch. Pharm.*, 1931, **269**, 581 ; Corrigan *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 1894 ; 1949, **71**, 530 ; Brown *et al.*, *ibid.*, 1948, **70**, 3738 : Dornow and Petsch, *Arch. Pharm* , 1952, **285**, 323). A review on their chemistry and pharmacology has been published in details by A. Burger ("Medicinal Chemistry", Interscience Publishers, Inc., New York, N.Y., 1951, Vol. I, p. 296).

The present authors have developed a simple method (*Science & Culture*, 1957, **23**, 155) for the synthesis of β-hydroxy-β-*p*-methoxyphenylethylamine. It has now been extended in the preparation of various other β-phenylethanolamines, *iso*quinoline alkaloids and other alkaloids which are acylamido-alcohol derivatives. The syntheses of papaverine, an alkaloid of *Papaver somniferum*, L. and aegeline, an alkaloid-amide occurring in the leaves of *Aegle marmelos* Correâ (Chatterjee, Bose and Srimany, *J. Org. Chem.*, 1959, **24**, 687) and several β-hydroxy-β-arylethylamines are described in this communication.

β-Phenylethanolamine derivatives (Table I) were synthesised by the addition of hydrocyanic acid to appropriate aldehydes when the corresponding cyanohydrins were formed. The latter were then smoothly reduced to β-phenylethanolamines with lithium aluminium hydride.

β-Hydroxy-β-*p*-methoxyphenylethylmethylamine (Table I) was prepared in a satisfactory yield by the hydrolysis of the methyl iodide addition product of the Schiff base of β-hydroxy-β-*p*-methoxyphenylethylamine and piperonal according to the method of Ray *et al.* (this *Journal*, 1937, **14**, 346). In an analogous way β-hydroxy-β-3 : 4-dimethoxy- and β-hydroxy-β-3 : 4-methylenedioxy-phenylethylmethylamines were synthesised.

TABLE I

β-Hydroxy-amines.	Mol. formula.	Yield.	M.P. of the hydrochlorides
*-β-*p*-methoxyphenylethyl-	$C_9H_{13}O_2N$	80%	173°
*-β-3 : 4-dimethoxyphenylethyl-	$C_{10}H_{15}O_3N$	72	163°
*-β-3 : 4-methylenedioxyphenyl-	$C_9H_{11}O_3N$	80	181-82°
‡-β-*p*-methoxyphenylethylmethyl-	$C_{10}H_{15}O_2N$	50	101°
*-β-3 : 4-dimethoxyphenylethylmethyl-	$C_{11}H_{17}O_3N$	46	143-45° (d.)
‡-β-3 : 4-methylenedioxyphenylethylmethyl-	$C_{10}H_{13}O_3N$	50	163 65° (d.)

* Solid.
‡ Liquid.

For the synthesis of papaverine, β-hydroxy-β-3 : 4-dimethoxyphenylethylamine hydrochloride was condensed with homoveratroyl chloride to yield homoveratroyloxy-homoveratrylamine. All attempts to isolate the latter from the reaction mixture were unsuccessful because of its high solubility in water. A suitable technique has been developed in isolating this amide, details of which have been described in the Experimental. Homoveratroyloxy-homoveratrylamine on subsequent ring-closure with phosphorus pentoxide in xylene afforded papaverine in good yield.

It was reported earlier by Chatterjee and Srimany ("Handbook of XVIth International Congress of Pure and Applied Chemistry," Part II, 1957, p. 199) that aegeline, the neutral compound occurring in the leaves of *Aegle marmelos* Correâ (Chatterjee and Bose, this *Journal*, 1952, **29**, 425) was an optically inactive alkaloid-amide and its structure and stereochemistry were established by them as *dl-trans-N*-(β-hydroxy-β-*p*-methoxyphenyl)-ethylcinnamamide from the studies of its various degradative experiments, synthesis and conformational analysis. A new synthesis of *dl*-aegeline has now been achieved by the present authors by reduction of anisaldehyde cyanohydrin with lithium aluminium hydride and subsequent condensation of the amine with *trans*-cinnamoyl chloride.

Although a considerable work has been performed to elucidate the structure and pharmacological activity of β-phenylethanolamines, much investigation is yet to be done in this field. As a part of this programme, pharmacological action of the compounds (vide Table I) is being studied in details to ascertain how and to what extent structural variation in β-arylethanolamines modifies their physiological properties, the results of which will be published in future.

EXPERIMENTAL*

Anisaldehyde cyanoyhydrin was prepared according to McCombie and Parry (*J. Chem. Soc.*, 1909, **95**, 584). The cyanohydrin crystallised from a mixture of benzene and petroleum ether (b.p. 60-80°) in stout rods, m.p. 67°, yield 70%. (Found : C, 66.30 ; H, 5.51 ; N, 8.62. Calc. for $C_9H_9O_2N$: C, 66.25 ; H, 5.52 ; N, 8.58%).

Veratraldehyde Cyanohydrin.—A solution of sodium bisulphite (200 g. in 200 c.c. of water) was added to veratraldehyde (50 g.), dissolved in alcohol (40 c.c.), cooled in a freezing mixture with vigorous stirring. The bisulphite compound was collected (after cooling) and washed with ether. A suspension of the latter in water (100 c.c.) was shaken with an aqueous solution of sodium cyanide (60 g. in 150 c.c. water), the reaction flask being cooled in the freezing mixture. The resulting cyanohydrin was extracted with ether (yield 50-52 g.). It was crystallised from acetone in shining needles, m.p. 110-12°. (Found : C, 62.23 ; H, 5.76 ; N, 7.38. Calc. for $C_{10}H_{11}O_3N$: C, 62.17 ; H, 5.69 ; N, 7.24%).

β-Phenylethanolamines.—The reduction of the aldehyde cyanohydrins with lithium aluminium hydride to the corresponding β-phenylethanolamine derivatives was carried out according to the method of Nace and Smith (*J. Amer. Chem. Soc.*, 1952, **74**, 1861) with some modifications.

* Melting and boiling points are uncorrected.

For the prepartion of the amines, a solution of the corresponding aldehyde cyanohydrin (6 g.) in dry ether (50 c.c.) was added dropwise to a slurry of lithium aluminium hydride (4 g.) in the same solvent (200 c.c.), the reaction mixture being cooled at 0°. Dry tetrahydrofuran was employed for reducing veratraldehyde cyanohydrin because of its poor solubility in dry ether. The reaction mixture in each case was kept stirred at ordinary temperature for 5 to 6 hours and then refluxed for 4 to 5 hours on a water-bath. The addition complex was decomposed by dropwise addition of water (5 c.c.), then aqueous sodium hydroxide (10 c.c., 20%) and finally by water (15 c.c.). The resulting product after refluxing for half-an-hour on the water-bath was filtered hot, washed with ether (150 c.c.) and the filtrate was dried over anhydrous potassium carbonate. The ether extract on evaporation yielded the desired amines. The hydrochlorides of the amines were obtained by saturating their anhydrous ethereal solutions with dry HCl gas, when the hydrochlorides separated out. These were purified by several crystallisations from acetone or from the same solvent diluted with water.

β-Hydroxy-β-p-methoxyphenylethylamine was crystallised from a mixture of benzene and petroleum ether (b.p. 40-60°), m.p. 70° (sealed tube). It was hygroscopic. The hydrochloride of the amine crystallised from acetone, containing a little water, in flakes, m.p. 173°. (Found: C, 53.16; H, 6.70; N, 6.92. Calc. for $C_9H_{13}O_2N.HCl$: C, 53.06; H, 6.87; N, 6.87%).

β-Hydroxy β-3:4-dimethoxyphenylethylamine.—The base is a pale yellow viscous oil, b.p. 180-82°/4 mm. Its hydrochloride crystallised from acetone in leaflets, m.p. 163°. (Found: C, 51.44; H, 6.78; N, 5.93. $C_{10}H_{15}O_3N.HCl$ requires C, 51.39; H, 6.85; N, 5.98%).

β-Hydroxy-β-3:4-methylenedioxyphenylethylamine.—The free base, a colorless viscous oil, was converted into its hydrochloride by the method described above. It crystallised from acetone in flakes, m.p. 181-82°. (Found: C, 49.72; H, 5.58; N, 6.33. Calc. for $C_9H_{11}O_3N.HCl$: C, 49.65; H, 5.51; N, 6.43%).

Piperonylidene-β-hydroxy-β-p-methoxyphenylethylamine.—The Schiff bases of the aforesaid amines were synthesised by refluxing equimolecular quantities of the amine and piperonal, dissolved in 95% ethanol, for an hour. The solvent was removed in *vacuo* and the product crystallised from various solvents. The yield varied from 90 to 95%.

This Schiff's base crystallised from a mixture of benzene and petroleum ether (60-80°) in colorless needles, m.p. 115-16°. (Found: C, 68.35; H, 5.76. $C_{17}H_{17}O_4N$ requires C, 68.23; H, 5.68%).

Piperonylidene-β-hydroxy-β-3:4-dimethoxyphenylethylmethylamine separated from a mixture of benzene and petroleum ether (60-80°) in colorless shining needles, m.p. 129-30°. (Found: C, 65.78; H, 5.94. $C_{18}H_{19}O_5N$ requires C, 65.65; H, 5.79%).

Piperonylidene-β-hydroxy-β-3:4-methylenedioxyphenylethylamine crystallised from alcohol in colorless needles, m.p. 155-56°. (Found: C, 65.23; H, 4.82. Calc. for $C_{17}H_{15}O_5N$: C, 65.16; H, 4.79).

β-Hydroxy-β-phenylethylmethylamines.—In these cases, Schiff's bases (3 g.) of the amines were dissolved in dry benzene (100 c.c.), which were refluxed at 100° with methyl iodide (5 c.c.) for 5 to 6 hours.

The methyl iodide adduct separated in all cases as sticky solids which were dissolved in hot water (20-25 c.c.) and treated with HCl (conc., 2-3 c.c.) The latter was warmed for an hour and the acid aqueous portion was thoroughly extracted with ether to remove piperonal produced during hydrolysis. The acid aqueous solution was subsequently basified with an aqueous solution of NaOH (30%) and extracted first with ether and then with chloroform. The combined extract after drying over anhydrous sodium sulphate was evaporated when β-hydroxy-β-phenylethylmethylamines were obtained, which were purified by distillation in *vacuo*.

β-Hydroxy-β-p-methoxyphenylethylamine hydrochloride crystallised from a mixture of acetone and ethyl acetate (1 : 1) in colorless needles, m.p. 101°. (Found : C, 55.43 ; H, 6.68 ; N, 6.32. $C_{10}H_{15}O_2N.HCl$ requires C, 55.17 ; H, 6.89 ; N, 6.43%).

β-Hydroxy-β-3 : 4-dimethyphenylethylmethylamine hydrochloride separated from acetone in flakes, m.p. 143-45° (decomp.). The hydrochloride of this amine was hygroscopic. (Found : C, 53.48 ; H, 6.70 ; N, 5.52. $C_{11}H_{17}O_2N.HCl$ requires C, 53.33 ; H, 6.86 ; N, 5.65%).

β-Hydyoxy-β-3 : 4-methylenedioxyphenylethylmethylamine was crystallised from acetone in shining needles, m.p. 163-65° (decomp.). (Found : C, 52 05 ; H, 5.72 ; N, 6.32. $C_{10}H_{13}O_3N.HCl$ requires C, 51.83 ; H, 5.61 ; N, 6.04%).

Homoveratroyloxy-homoveratrylamine.—To homoveratric acid (5 g.), dissolved in the minimum quantity of chloroform, thionyl chloride (7 c.c.) was added. After gently boiling for 2 hours on a water-bath, the chloroform was distilled off. Homoveratroyl chloride (3 g.) was added to β-hydroxy-β-3 : 4-dimethoxyphenylethylamine hydrochloride (2 g.), dissolved in the minimum quantity of water, and stirred vigorously for 2 hours after adding an excess of KOH (1.5 g). During stirring a yellow gummy mass separated out, which was decanted off and washed twice with a little water. The reaction product was next dissolved in the minimum quantity of alcohol containing a few drops of dilute NaOH solution and left for a day, when a yellow solid was deposited. This was crystallised several times from benzene in shining rods, m.p. 127-28°, yield 2 g. (Found : C, 64.08 ; H, 6.76 ; N, 3.92. $C_{20}H_{25}O_6N$ requires C, 64.00 ; H, 6.66 ; N, 4.00%).

Synthesis of Papaverine.—Homoveratroyloxy-homoveratrylamine (2 g.) was dissolved in warm and dry xylene. The solution was refluxed with P_2O_5 (10 g.) for 5 mins. After decanting off the xylene, the light yellow residue left at the bottom was treated with ice-cold water, when it dissolved. The solution was extracted with ether. The aqueous acidic portion was withdrawn and made alkaline with concentrated sodium hydroxide solution when an emulsion was formed, which was kept for a day. Solids deposited were filtered and crystallised from a mixture of chloroform and petroleum ether in shining star-shaped needles, m.p. 147°, yield 0.51 g.. (Found : C, 70.85 ; H, 6.32 ; N, 4.36. Calc. for $C_{20}H_{21}O_4N$: C, 70.79 ; H, 6.19 ; N, 4.10%).

Its mixed melting point with an authentic sample of papaverine remained undepressed.

Synthesis of Aegeline.—*trans*-Cinnamoyl chloride (3 g.), dissolved in dry ether (15 c.c.), was added dropwise to β-hydroxy-β-*p*-methoxyphenylethylamine (2 g.), taken in the same solvent (50 c.c.), with vigorous stirring when *dl-trans-N*-(β-hydroxy-β-*p*-methoxyphenyl)-ethylcinnamamide formed spontaneously separated out. The reaction product was subsequently made alkaline with a dilute solution of NaOH. The amide was filtered and washed several times with water. It was crystallised from ethyl acetate in shining needles, m.p. 177-78°, yield 1.2 g. (Found: C, 72 64; H, 6.26; N, 4.76; OMe 10.46. Calc. for $C_{18}H_{19}O_3N$: C, 72.72; H, 6.39; N, 4.71; OMe, 10.44%).

The synthetic amide was found identical with natural aegeline from their mixed melting point and comparison of their infra-red absorption spectra.

The authors take this opportunity to express their grateful thanks to Dr. Leo Marion, Director, National Research Council, Ottawa, Canada, for I. R. spectra of aegeline, to Mr. W. Manser, E.T.H., Zürich, Switzerland, and Mrs. C. Dutta, University College of Science, Calcutta, for microanalyses. Thanks are also accorded to the Council of Scientific & Industrial Research, India, for financing the research scheme and for the award of a Research Assistantship to one of them (N.A.C.).

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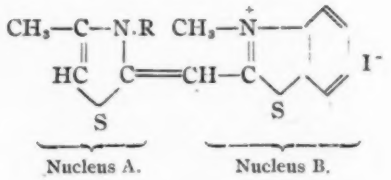
UNSYMMETRICAL METHIN CYANINES DERIVED FROM 4-METHYL-3-ARYL-1:2-DIHYDROTHIAZOLE-2-THIONE

By Pranabandhu Tripathy and M. K. Rout

Several unsymmetrical methin cyanines, derived from 4-methyl-3-aryl-1:2-dihydrothiazole-2-thione as the fixed component and four other basic nuclei as the variable component, have been prepared and their absorption maxima measured.

In the present work, investigations have been undertaken to determine the basicity of some nuclei. Unsymmetrical methin cyanines with 3-substituted 4-methylthiazole as the fixed component and one of the following : (1) 2-methylbenzoxazole, (2) lepidine, (3) 4-phenyl-2-methylthiazole, (4) 2-methylbenzimidazole and (5) quinaldine as the second variable component have been prepared and their absorption spectra as well as sensitisation spectra determined.

The unsymmetrical methin cyanines were prepared by the action of 3-phenyl-(or *o*-tolyl-, *m*-tolyl- or *p*-bromophenyl) 4-methyl-1:2-dihydrothiazole-2-thione on each of the above variable heterocyclic compounds (1-5) in presence of methyl *p*-toluenesulphonate (2 mol.), as described in the Experimental. The unsymmetrical methin cyanines have the general structure :



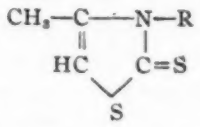
[R = Phenyl, *o*-tolyl, *m*-tolyl or *p*-bromophenyl. Nucleus B = benzoxazole-2 ; 4-phenylthiazole-2 ; benzimidazole-2 ; quinoline-4 or quinoline-2].

Experimental

3-Aryl-4-methyl-1:2-dihydrothiazole-2-thione : *3-Phenyl-4-methyl-1:2-dihydrothiazole-2-thione*.—To ammonium phenyldithiocarbamate (4.7 g.), suspended in ethanol (12 c.c.), monochloroacetone (12 c.c.) was added portionwise with cooling. The mixture was refluxed for 40 minutes and then diluted with water. The crystals which separated were filtered and washed with water. (In some cases oil separated, which crystallised out on keeping in contact with methanol). Finally it was crystallised from ethanol as brownish needles, m.p. 149°, yield 82%. (Found : S, 30.7. $C_{10}H_9NS_2$ requires S, 30.9%).

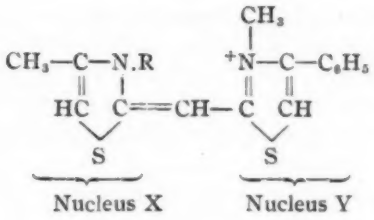
The properties and analytical data of other compounds of the series are recorded in Table I.

TABLE I



No.	Nature of R.	Yield.	M.P.	% Sulphur. Found.	Calc.
1.	*p*-Br.C_6H_4	67%	98°	20.54	20.64
2.	*p*-CH_3.C_6H_4-	81	135°	29.08	28.95
3.	*o*-CH_3.C_6H_4-	82	105°	28.70	28.95

TABLE II



No.	Nature of R in nucleus X.	Nature of the heterocyclic nucleus Y.	Yield.	$\lambda_{max.}$	M.P.	%Carbon Found.	%Carbon Calc.	%Hydrogen. Found.	%Hydrogen. Calc.
1.	Phenyl	A	50%	410 mμ	243° (d)	52.50	52.77	3.82	3.9
2.	,,	B	62	520	258° (d)	55.36	55.20	3.92	4.1
3.	,,	C	55	440	220°	51.35	51.40	3.80	3.9
4.	,,	D	78	335	240° (d)	51.90	52.06	4.20	4.3
5.	*p*-Bromophenyl	C	65	440	220° (d)	44.00	44.20	2.98	3.1
6.	,,	B	72	520	275° (d)	46.80	46.90	3.10	3.3
7.	,,	E	70	480	292° (d)	46.73	46.90	3.10	3.3
8.	,,	A	60	410	170° (d)	44.50	44.60	2.80	3.1
9.	*p*-Tolyl	A	68	410	239°	51.90	51.90	3.80	4.1
10.	*o*-Tolyl	A	73	410	247°	51.80	51.90	3.86	4.1
11.	*o*-Tolyl	E	68	480	249°	55.80	55.90	4.30	4.4
12.	*p*-Tolyl	E	63	480	201°	55.70	55.90	4.20	4.4
13.	*o*-Tolyl	B	62	520	188°	55.78	55 90	4.30	4.4
14.	*p*-Tolyl	B	60	520	195°	55.80	55.90	4.10	4.4
15.	*p*-Tolyl	C	52	440	215-16°	52.10	52.30	4.00	4.1
16.	*o*-Tolyl	C	50	440	243°	52.00	52.30	4.00	4.1

A = 3-Methylbenzoxazole. B = 1-Methyl-4-quinoline. C = 4-Phenyl-3-methylthiazole. D = *N*-methylbenzimidazole. E = 1-Methyl-2-quinoline.

Preparation of the Dyes.—The unsymmetrical methin cyanines were prepared by one of the two methods described below.

Method (I).—The appropriate 3-aryl-4-methyl-1 : 2-dihydrothiazole-2-thione (1*M*) and methyl *p*-toluenesulphonate (1.1*M*) were fused at 130° for 4 hours. Similarly, another fusion was carried out with the variable heterocyclic compound and methyl *p*-toluenesulphonate. The two compounds, thus prepared, were dissolved in pyridine and refluxed for 40 minutes. The reaction mixture was poured into a hot solution of KI (10 g./100 c.c.). In most cases oils separated, which solidified after washing with ether, water and hot benzene.

Method (II).—In the second method, molecular proportions of 4 methyl-3-aryl-1 : 2-dihydrothiazole-2-thione and the appropriate 2-methyl heterocyclic compound were taken together. To this methyl *p*-toluenesulphonate was added and the whole fused at 140° for 4 hours. On cooling, pyridine (25 c.c.) was added to it. The reaction mixture was refluxed for 40 minutes. The dye iodides were prepared as in the previous method. The preparation and properties are recorded in Table II.

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TRIHALOGENATED NITROBENZENES AND THEIR DERIVATIVES. PART III

By R. S. Kapil and Shiam Sunder Joshi

The preparation of four trihalogenated benzenes, their nitration and structure are described.

Earlier papers of this series described the nitration of 1 : 2 : 4-(Joshi and Gupta, this *Journal*, 1952, **29**, 193) and 1 : 2 : 3-(Joshi and Saxena, *ibid.*, 1953, **30**, 548) trihalogenated benzenes. The present communication describes the nitration of 1-chloro-2 : 4-dibromo-, 1-chloro-3 : 4- and -3 : 5-dibromo- and 1 : 3-dichloro-5-bromobenzenes (Hurtley, *J. Chem. Soc.*, 1901, **79**, 1293), which have been prepared from the corresponding anilines by the replacement of an amino group by a halogen atom or by deamination.

In dinitration of 1-chloro-3 : 5-dibromo- and 1 : 3-dichloro-5-bromobenzenes, each can be expected to furnish two products; only one product has been isolated in each case, *i.e.*, 1-chloro-3 : 5-dibromo-2 : 6-dinitro- and 1 : 3-dichloro-5-bromo-2 : 6-dinitrobenzenes. The structure of 1-chloro-3 : 5-dibromo-2 : 6-dinitrobenzene has been established by (*i*) replacing one of the halogen atoms by a hydroxyl group (Borsche, *Ber.*, 1917, **50**, 1350) when 3-chloro-5-bromo-2 : 4-dinitrophenol is formed (Kohn and Zandman, *Monatsh.*, 1926, **47**, 357) and (*ii*) by replacing the two bromine atoms by methoxyl groups, when a product identical with the one similarly obtained from 1 : 3 : 5-trichloro-2 : 6-dinitrobenzene, *i.e.*, 1-chloro-3 : 5-dimethoxy-2 : 6-dinitrobenzene (Schlubach and Mergenthaler, *Ber.*, 1925, **58B**, 2735), is obtained.

Similarly, the structure of the only product, isolated by dinitration of 1 : 3-dichloro-5-bromobenzene, appears to be 1 : 3-dichloro-5 bromo-2 : 6-dinitrobenzene, as dimethoxy and di-*p*-toluidino derivatives obtained from it, and from 1-chloro-3 : 5-dibromo-2 : 6-dinitrobenzene [viz., 1-chloro-3 : 5-dimethoxy-(or di-*p*-toluidino)-2:6-dinitrobenzene ; Borsche and Trautner, *Annalen*, 1926, **447**, 1)] are identical.

Dinitration of 1-chloro-2 : 4-dibromo- and 1-chloro-3 : 4-dibromobenzenes affords respectively 1-chloro-2 : 4-dibromo- 3 : 5-dinitro- and 1-chloro-3 : 4-dibromo-2 : 6-dinitrobenzenes. Their identity has been established by preparation of anilino and *p*-toluidino derivatives, *i.e.*, 1-chloro 2 : 4-dianilino-(or *p*-toluidino)-3 : 5-dinitro- and 1 bromo-2 : 4-dianilino-(or *p*-toluidino)-3 : 5-dinitrobenzenes (Joshi and Gupta, *loc. cit.*).

2 : 4-Dibromoacetanilide has been obtained in better yields by direct bromination of *o*-bromoacetanilide rather than by earlier methods (Chattaway and Clemo, *J. Chem. Soc.*, 1916, **109**, 91 ; Chaudhri *et al.*, this *Journal*, 1934, **11**, 254 ; Thomassin, *Compt. rend.*, 1946, **222**, 503).

Experimental*

** 2 : 4-*Dibromoacetanilide.*—*o*-Bromoacetanilide (10 g.), dissolved in glacial acetic acid, was treated dropwise with a calculated quantity of bromine, dissolved in

* All melting points given are uncorrected.
** Prepared before.

acetic acid, with vigorous shaking. After keeping the product for an hour, it was diluted with water, when 2:4-dibromoacetanilide separated in a crystalline form (90%). It was crystallised from alcohol in colorless needles, m p. 146°.

** 3:4-*Dibromoacetanilide* was similarly prepared from *m*-bromoacetanilide in colorless needles from alcohol, m.p. 128°.

** 2:4- & 3:4-*Dirbomoanilines* were prepared by hydrolysis of the corresponding acetanilides by heating with H_2SO_4 (conc.) for 4 hours in alcoholic solution.

** 2:4- & 3:4-*Dibromo-1-chlorobenzenes* were prepared by subjecting the respective anilines to Sandmeyer's reaction to replace the amino group by a chlorine atom.

1-*Chloro*-3:5-*dibromo*-2:6-*dinitrobenzene*.—To a cooled suspension of 1-chloro-3:5-dibromobenzene (10 g.) in H_2SO_4 (42 c.c., *d* 1.82), fuming nitric acid (28 c.c., *d* 1.5) was added dropwise with vigorous stirring. When all the nitric acid had been added, the mass was heated on a water-bath for about 4 hours. It was cooled and poured on ice. The nitrated product separating was crystallised from alcohol or acetic acid in colorless needles (80%), m.p. 176°.

Similarly, the other trihalogenated dinitrobenzenes were prepared from trihalogenated benzenes (Table I).

TABLE I

No.	Halogeno-benzene used.	Halonitrobenzene formed.	M.P.	Colour.	Formula.	% Cl + Br. Found.	Calc.
1.	1-Chloro-3:5-di-B	1-Chloro-3:5-di-bromo-2:6-D	176	Colorless needles	$C_6HO_4N_2ClBr_2$	53.84	54.19
2.	1:3-Dichloro-5-B	1:3-Dichloro-5-bromo-2:6-D	151	Colorless cubes.	$C_6HO_4N_2Cl_2Br$	47.62	47.74
3.	1-Chloro-2:4-di-B	1-Chloro-2:4-dibromo-3:5-D	133	Pale yellow needles	$C_6HO_4N_2ClBr_2$	53.68	54.19
4.	1-Chloro-3:4-di-B	1-Chloro-3:4-dibromo-2:6 D	125	Pale yellow needles	$C_6HO_4N_2ClBr_2$	54.01	54.19

[B = bromobenzene. D = dinitrobenzene].

** 3-*Chloro*-5-*bromo*-2:4-*dinitrophenol*.—A mixture of 1-chloro-3:5-dibromo-2:6-dinitrobenzene (1 g.), anhydrous sodium acetate (1 g.) and acetamide (3 g.) was kept at 160-80° for 2 hours. It was then dissolved in strong ammonia (15 c.c.) with charcoal (0.5 g.) and heated further for 3 hours. The filtrate on acidification yielded the phenol (0.3 g.). It was recrystallised from alcohol in yellow crystals, m.p. 97°.

** 1-*Chloro*-3:5-*dimethoxy*-2:6-*dinitrobenzene*.—1-Chloro-3:5-dibromo-2:6-dinitrobenzene was heated with twice the equivalent quantity of sodium methoxide in methyl alcohol for an hour. On cooling, crystals of the product separated. It was recrystallised from methyl alcohol, m.p. 218°

** 3:5-*Di*-p-*toluidino*-1-*chloro*-2:6-*dinitrobenzene*.—A mixture of 1-chloro-3:5-dibromo-2:6-dinitrobenzene with twice the equivalent quantity of *p*-toluidine and

anhydrous sodium acetate in alcohol was refluxed on a water-bath for an hour. The product separating was recrystallised from acetic acid as red crystals, m.p. 231°.

** 1-*Chloro*-2 : 4-*dianilino*-(*or* p-*toluidino*)-3 : 5-*dinitrobenzene*.—1 - Chloro-2 : 4-dibromo-3 : 5-dinitrobenzene on heating with aniline or *p* toluidine, as described above, furnished the corresponding orange-red anilino or *p*-toluidino derivative ; dianilino, m.p. 187° ; di-*p*-toluidino, m.p. 177°.

** 1-*Bromo*-2 : 4-*dianilino*-(*or* p-*toluidino*)-3 : 5-*dinitrobenzene* was also prepared by the above procedure from aniline or *p*-toluidine and 1-chloro-3 : 4-dibromo-2 : 6-dinitrobenzene ; dianilino, m.p. 192° ; di-*p*-toluidino, m.p. 204°.

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SHORT NOTES

POLYPHOSPHORIC ACID AS A CONDENSING AGENT IN THE PECHMANN REACTION

By R. S. Kapil and Shiam Sunder Joshi

A variety of condensing agents such as sulphuric acid (Pechmann and Duisberg, *Ber.*, 1883, **16**, 2119), zinc chloride (Pechmann and Schaal, *Ber.*, 1899, **32**, 3690), hydrogen chloride (Bülow, *Ber.*, 1905, **38**, 474), phosphorus pentoxide (Petschek and Simonis, *Ber.*, 1913, **46**, 2014), phosphorus oxychloride (Naik, Desai and Desai, this *Journal*, 1929, **6**, 83), phosphoric acid (Chakravarti, *ibid.*, 1935, **12**, 536), aluminium chloride (Sethna, Shah and Shah, *J. Chem. Soc.*, 1938, 228), etc. have been used in the Pechmann reaction. Recently polyphosphoric acid (Koo, *Chem. & Ind.*, 1955, 445) has also been used in this reaction.

In this communication the reaction of ethyl acetoacetate with a number of phenols in presence of polyphosphoric acid has been studied. In all cases studied, only coumarins have been isolated. The results obtained shows that it is a better condensing agent than concentrated sulphuric acid in as much as higher yields of purer products are obtained.

Procedure.—Polyphosphoric acid was prepared according to the method of Sukh Dev (this *Journal*, 1955, **32**, 255). A mixture of polyphosphoric acid and phenol in the proportion of 15 : 1 was used in the condensation. The reaction was completed by heating on a water-bath for 30 minutes. The product was isolated in the usual manner. The coumarins prepared by this method are listed in Table I.

Table I

No.	Coumarin obtained.	Phenol used.	% Yield.	M. P.
1.	4 :7-Dimethyl-	*m*-Cresol	35	132°
2.	4 :6-Dimethyl-	*p*-Cresol	40	152°
3.	4-Methyl-7 :8-benzo-	α-Naphthol	85	172°
4.	7-Hydroxy-4-methyl-	Resorcinol	96	185°
5.	7-Hydroxy-6-chloro-4-methyl-	4-Chlororesorcinol	66	280°
6.	5-Hydroxy-4 :7-dimethyl-	Orcinol	90	250°
7.	7 :8-Dihydroxy-4-methyl-	Pyrogallol	50	235°
8.	5 :7-Dihydroxy-4-methyl-	Phloroglucinol	62	285°

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FREEZING POINTS OF THE BINARY MIXTURES. β-PICOLINE-γ-PICOLINE, β-PICOLINE-2:6-LUTIDINE AND γ-PICOLINE-2:6-LUTIDINE

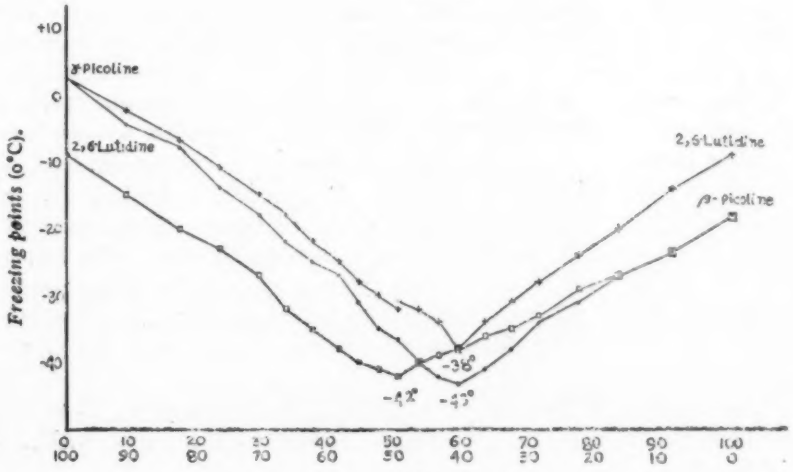
By A. M. Tyabji

The freezing point curves of the binary mixtures mentioned in the title were determined with a view to evolving a quick method of estimating the purity of specimens of the bases obtained by various technical methods. The data supplied by Coulson and Jones (*J. Soc. Chem. Ind.*, 1946, **65**, 169) have thus been extended over a wider range, and the results of this simple method agree well with those found by the more elaborate U.V. absorption methods.

The bases used by us had the following freezing points: γ-picoline 2.5° (4.3°), β-picoline −18° (−17.7°), 2:6-lutidine −9° (−5.9°). The numbers in parentheses refer to the freezing points recorded by Coulson and Jones (*loc. cit.*).

Procedure.—To 10 c.c. of the one component were added successive quantities of 1 c.c. of the second component. The mixture was then frozen in solid CO_2 . ether with constant stirring, an alcohol thermometer being used. The crystals were then allowed to melt slowly with continuous stirring and the point of complete liquefaction determined repeatedly. The procedure was repeated after the next addition and so on till a total volume of 20 c.c. had been attained, when the experiment was terminated and a fresh start made with 10 c.c. of the second component. Thus the 50% mixture composition was approached from both sides. The results are represented in the form of a graph in Fig 1.

Fig. 1



The eutectic points are noteworthy, as also the fact that up to 2 c.c. additions of either 2:6-lutidine or γ-picoline gave identical depressions of the freezing point of β-picoline.

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CONDENSATION OF METHYLSUCCINIC ANHYDRIDE WITH CHLOROBENZENE

By D. K. Genge and J. J. Trivedi

The reaction between an aromatic compound and a mono-substituted succinic anhydride can give rise to two isomeric aroylpropionic acids, one of which is usually formed in small quantity (Adams, "Organic Reactions", Vol. V, p. 242). Methylsuccinic anhydride, when allowed to react with an excess of chlorobenzene, furnished a product, m.p. 118°, after purification through its semicarbazone. This product has been proved to be β-*p*-chlorobenzoyl-α-methylpropionic acid as it does not depress the m.p. of a synthetic sample of the latter. β-*p*-Chlorobenzoyl-α-methylpropionic acid has been synthesised from *p*-chloro-ω-bromoacetophenone and sodium derivative of ethyl methylmalonate.

Condensation of Methylsuccinic Anhydride with Chlorobenzene.—A mixture of chlorobenzene (120 g.), methylsuccinic anhydride (11.4 g.) and anhydrous aluminium chloride (15 g.) was heated with usual precautions on a water-bath for 5 hours, and the keto-acid (5 g.) was isolated by the usual method after steam-distilling off chlorobenzene. This was converted into its semicarbazone which was hydrolysed by acid, and the β-*p*-chlorobenzoyl-α-methylpropionic acid crystallised from hot water, m.p. 118°. It did not depress the m.p. of a genuine sample of the acid synthesised (*vide infra*). (Found : N.E. 228.0 ; Cl, 15.5. Calc. for $C_{11}H_{11}O_3Cl$: N.E. 226.5 ; Cl, 15.7%).

Synthesis of β-p-*Chlorobenzoyl-α-methylpropionic Acid.*—To a cold solution of *p*-chloroacetophenone (10 g.) in chloroform (50 c.c.) a solution of bromine (3 c.c. in 10 c.c. of chloroform) was added dropwise and afterwards the mixture was kept at room temperature for 3 hours. HBr was removed by drawing a slow current of air through the solution for an hour. *p*-Chloro-ω-bromoacetophenone crystallised out on removal of chloroform, m.p. 96° (Collet, *Bull. soc. chim.*, 1874, *iii*, **21**, 69, records m.p. 96°-96.5°).

To a cold suspension of sodium powder (0.33 g.) in dry benzene (5 c.c.) ethyl methylmalonate (5 g.) was added and the mixture was refluxed on a water-bath for 4 hours. After cooling, *p*-chloro-ω-bromoacetophenone (4 g.) in benzene (25 c.c.) was added and the mixture refluxed for 4 hours. After removing benzene the residue was refluxed with 10% methanolic KOH (50 c.c.) for 3 hours. Alcohol was removed, the residue acidified with HCl, the liberated acid extracted with ether, ether evaporated, and finally the residue was decarboxylated by heating at 180° for half an hour. The product obtained was treated with sodium bicarbonate solution, the clear solution acidified and the liberated β *p*-chlorobenzoyl-α-methylpropionic acid was crystallised from hot water, m.p. 118°.

The *semicarbazone* of the acid was prepared by the usual method. It was crystallised from dilute alcohol, m.p. 165° (decomp.). [Found : N.E., 285.0. $C_{12}H_{14}O_3N_3Cl$ requires N.E., 283.5].

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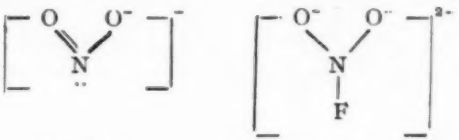
MONOFLUORONITRITE

By Asim Bikash Ray and Amiyakanti Ghosh

No fluoro- or oxyfluoro-acid of nitrogen is known till now. The fluorides of nitrogen are themselves very peculiar. Nitrogen trifluoride, for example, is surprisingly inactive and is not acted upon by a number of substances even at elevated temperatures (Ruff *et al.*, *Z. anorg. Chem.*, 1928, **172**, 417 ; 1931, **197**, 273). This inactivity of nitrogen trifluoride is one of the reasons ascribed to non-isolability of the oxyfluoro- or fluoro-acids of nitrogen. Other important fluorides of nitrogen are NF_2 and N_2F_2 (Ruff *et al.*, *ibid.*, 1931, **198**, 32 ; 1934, **217**, 93). These lower fluorides present interesting structural problems.

Nitrogen forms two oxyfluoro compounds, NO_2F and NOF, which are obtained by the replacement by fluorine of hydroxyl groups of nitric and nitrous acids. The remarkable compound, fluorine nitrate, NO_3F, demands special attention (Cady, *J. Amer. Chem. Soc.*, 1934, **56**, 2635). The isolation of fluorine nitrate shows that the possibility of isolation of oxyfluoronitrate is very meagre. On the other hand, in nitrous acid one of the orbitals of nitrogen is still vacant and, hence, the possibility of isolation of oxyfluoro-acid of nitritic nitrogen is high. This fact has been realised.

The structure of the complex ion in keeping with the above argument should be :



[Nitrite ion] [Oxyfluoro ion (p^3 hybridisation)]

The above structure shows that the complex ion should be bivalent negative containing neutral trivalent nitrogen atom. The isolation of the potassium salt confirms this view. It is interesting to note that the salt crystallises with one molecule of hydrofluoric acid, indicating the possibility of a hydrogen bond between the nitrogen and the fluorine atom of HF. Similar observation was made in the case of NH_4HF_2 and water ("Sidgwick, "Chemical Elements and their Compounds", Oxford, 1950, Vol. I, p. 705).

Method of Estimation.—Potassium was estimated as sulphate, nitrogen as ammonia by distillation with alkaline zinc dust and fluorine as CaF_2 after decomposing the sample with sodium carbonate.

N_2O_3 (gas), obtained by heating HNO_3 (conc.) and As_2O_3, was passed through a fairly concentrated solution of KF in a glass basin at room temperature. The passage of the gas was continued till the solution became saturated with N_2O_3 and copious evolution of brown fumes was observed. The solution at that time turned acid to

litmus. It was then allowed to crystallise in a sulphuric acid desiccator. After a few days long, needle-shaped, colorless crystals were obtained. (Found : K, 48.50 ; N, 8.62 ; F, 23.40. $K_2NO_2F.HF$ requires K, 47.91 ; N, 8.57 ; F, 23.28%).

$$4KF + N_2O_3 + H_2O = 2K_2NO_2F.HF.$$

The X-ray data of the powdered picture of the salt are recorded in Table I.

TABLE I

d.	*Intensity.	*d.*	Intensity.	*d.*	Intensity.	*d.*	Intensity.	*d.*	Intensity.
4.60Å	M	2.330Å	W	1.881Å	W^-	1.551Å	W	1.271Å	W^{--}
3.750	S	2.184	M^+	1.764	W	1.521	W^+	1.256	W^{--}
3.020	M^+	2.151	W^{++}	1.703	W	1.400	W	1.245	W^{--}
2.764	M	2.053	W^{++}	1.681	W	1.380	W^-	1.185	W^{--}
2.640	M^{++}	1.999	W^-	1.625	W	1.352	W^+	1.147	W^{--}
2.403	W	1.943	M	1.585	W	1.330	W		

*(Cu-K_α radiation).

Properties.—The salt on heating in a test-tube melts without any evolution of brown fumes. However, vapours of hydrofluoric acid are given off and the residue responds to tests of nitrogen and fluorine. The *p*H of a saturated solution of the salt is 4. The crystals are non-hygroscopic unlike KNO_2 or KF. The salt can be recrystallised from water and the above analytical data are those of a recrystallised product. An equimolecular mixture of KNO_2 and KF or KHF_2 does not give rise to the above salt.

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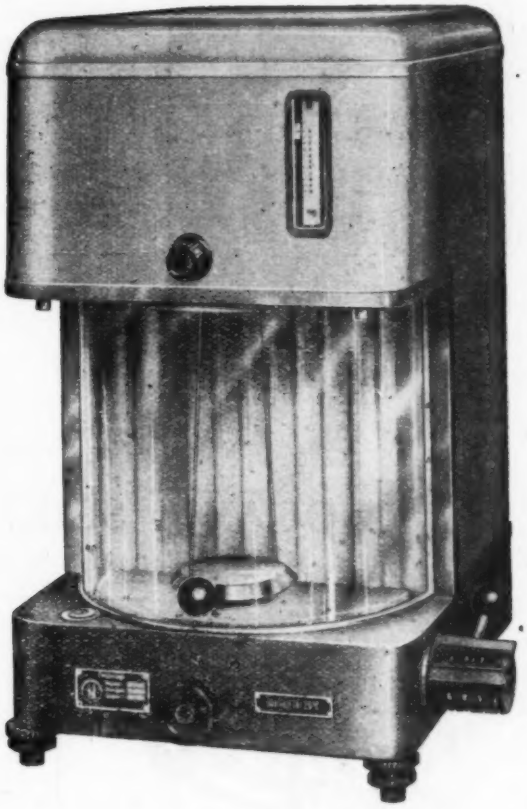

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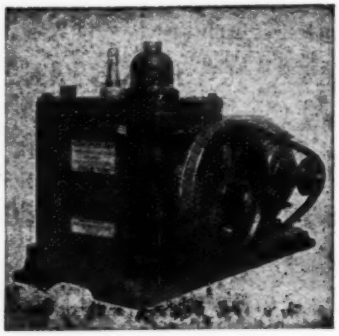

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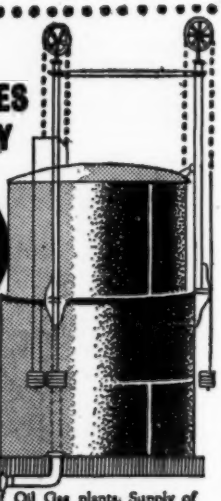

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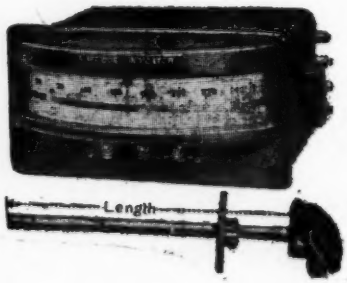

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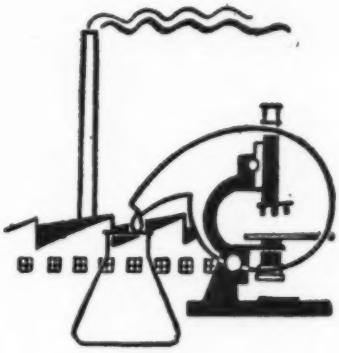

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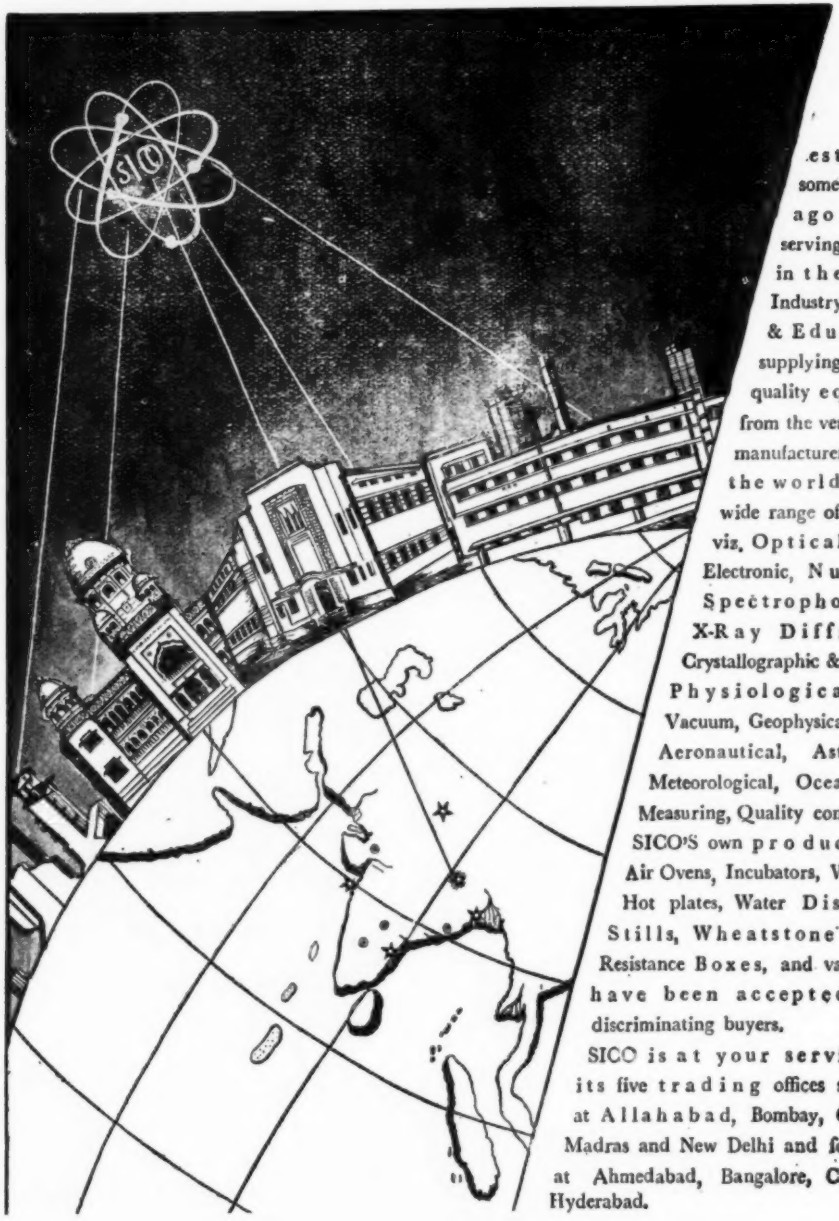

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